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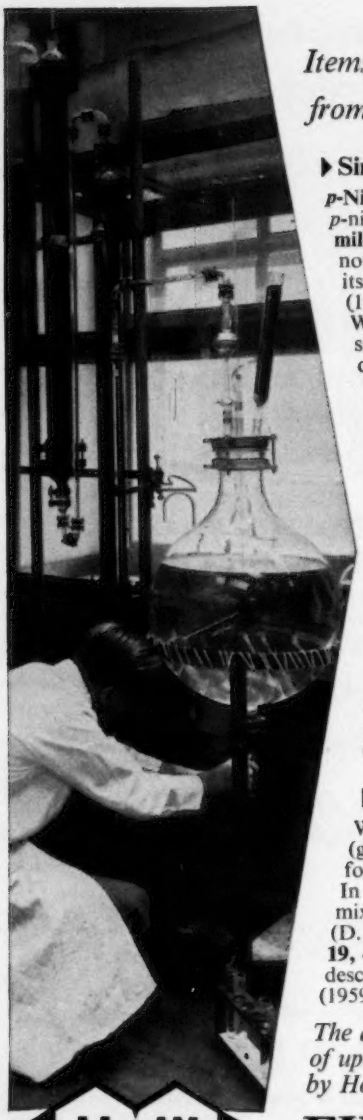

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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

General reviews of progress, reagents and methods of general application.

409. **Proceedings of the Seventh Spectrochemical Seminary.** June 15 to 18, 1959. Varese, Italy. *Metallurg. Ital.*, 1960, **15** (6), 272–386.—The following papers (in Italian unless otherwise stated) are of particular analytical interest. **The influence of spectroscopic carbons on spectroanalytical problems,** H. Rüssmann, pp. 280–288 (in French). **Research and technical spectrophotometry,** L. Riccoboni, pp. 289–305. **The present position of X-ray fluorescence spectrometry,** A. Giavino, pp. 306–314. **Spectrography of trace elements in lead of high purity,** A. Bianchini and L. Zanaroli, pp. 315–319. **A spectrographic method for the analysis of aluminosilicate refractories,** A. Porta, pp. 320–325. **Spectrographic analysis of Al - Cu alloys,** E. Raiteri, pp. 326–330. **Determination of phosphorus in steel by direct spectral analysis by the use of the Quantometer ARL 1·5m PCQ n. 7200,** G. Bianchi, pp. 331–335. **A new organic reagent for the determination of copper in bauxite and derived products,** M. F. Landi, pp. 336–340. **Use of spectrophotometry in the analysis of steel. II. Determination of manganese, nickel, molybdenum, niobium, tantalum, tungsten, titanium, vanadium, cobalt and copper,** A. Sommariva and D. Devoti, pp. 341–354. **Spectrophotometric determination of antimony in copper alloys,** M. L. Foglino, pp. 355–357. **Spectrophotometric determination of phosphorus in steel, cast iron and ferrous minerals,** G. Picasso, pp. 358–365. **The fluorimetric determination of gallium,** M. L. Landi, pp. 366–371.

410. **Analysis for industry.** A. M. G. Macdonald. *Ind. Chem.*, 1960, **36**, 292–294.—Recent developments in the Karl Fischer procedure are described. (28 references.) S.C.I. Abstr.

411. **Ultra-micro chemical analysis.** M. Ördögh. *Magyar Kém. Lapja*, 1960, **15** (7), 325–329.—A literature survey is presented with 53 references. R. E. E.

412. **The problem of destruction and enrichment in micro-analysis.** E. Schulek and J. Laszlovszky (Inst. f. anal. Chem., L. Eötvös Univ., Budapest, Hungary). *Mikrochim. Acta*, 1960, (4), 485–501 (in German).—Problems of sample preparation for micro-analysis are reviewed. Materials recommended for dissolution are, as reducing agents, H_2O_2, ethanol, hydrazine or H_2S, and, as oxidants, H_2O_2 and NH_4NO_3. For fusions or saponification the purer KOH (of known halide content) is preferred to NaOH and for wet-oxidation H_2O_2 - H_2SO_4 to HNO_3 and to $HClO_4$ (large amounts of organic matter being first destroyed with HNO_3). Enrichment of trace quantities in large samples by complex formation and extraction, particularly with $CHCl_3$ or CCl_4 in funnels of special shape, is recommended. Other methods, *e.g.*, evaporation, distillation, adsorption on carbon or ion exchangers and paper chromatography, are mentioned. J. P. Stern

413. **Adsorption by finely divided particles of strongly basic anion exchangers at the interface between two immiscible liquids, and its application to microchemical analysis.** Masatoshi Fujimoto (Chem. Inst., Sci. Fac., Univ. of Tokyo, Japan). *Naturwissenschaften*, 1960, **47** (11), 252 (in German).—Development of the 'resin-drop' method (*cf. Chemist Analyst*, 1960, **49**, 4) has led to the investigation of the phenomenon described. A very dilute soln. of sample is shaken with a small volume of an immiscible solvent in the presence of the anion exchanger. The substance to be determined is concentrated at the liquid interface, on the surface of the resin, and the materials are chosen so as to provide a sensitive colour reaction and thus facilitate an otherwise difficult determination. E. G. Cummins

414. **The inter-laboratory evaluation of testing methods.** J. Mandel and T. W. Lashof (A.S.T.M., 1916 Race Street, Philadelphia, Pa., U.S.A.). *Bull. A.S.T.M.*, 1959, (239), 53–61.—The sources of the variable results from laboratories adopting a particular method are examined. The systematic differences are related linearly to the numerical magnitude of the measurements (by the same observer at different times or on different instruments, or by different observers in the same or different laboratories) and can be represented by a linear model. In this model the total error is segregated into the components of replication, namely, scatter and inter-laboratory variation, and the relative contributions of these components to the total variance of the values are determined. The design, analysis and interpretation of a 'round-robin' test in accordance with this linear model are fully described, and the procedure is illustrated by an analysis of data obtained with the Beck smoothness tester for paper, in 14 laboratories each testing 14 different samples. Although complex, the model is claimed as an improvement on the usual two-way analysis of variance, because it provides for all random and non-random differences originating from laboratories, from materials and from the interaction of these two sources. W. J. Baker

415. **Calculation of errors of indirect analyses.** L. Erdey and G. Svehla (Inst. for Gen. Chem., Tech. Univ., Budapest). *Z. anal. Chem.*, 1960, **176** (1), 8–16 (in German).—The error involved in an indirect analysis (*e.g.*, of Na plus K weighed as chlorides and converted into AgCl) is shown mathematically to be a function of the error in the individual determinations, of the stoicheiometric conversion factors, and of the relative amounts of the components. Thus a small error in the analysis is favoured by a small error in either weighing, a high mol. wt. for the second weighing form (AgCl) and a low mol. wt. for the components of the first weighing form (NaCl, KCl) and a large difference between them. A simple expression gives the ratio of the two elements for which the error is a minimum. The error of an indirect analysis exceeds that of the individual determinations by several orders of magnitude. J. H. Waton

416. **The role of glass in chemical analysis.** J. P. Williams (Res. and Devel. Div., Corning Glass Works, Corning, New York, U.S.A.). *Microchem. J.*, 1960, **4** (2), 187–193.—The thermal properties, acid and alkali resistance, trace-metal content and spectral transmittance of 6 different glasses are reviewed. P. D. PARR-RICHARD

417. **Thionol as reagent for the micro-determination of bivalent tin and chromium and tervalent titanium.** E. Růžička (Dept. Chem., Fac. Sci., Palacký Univ., Olomouc, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1960, **25** (6), 1691–1694 (in Russian).—The red soln. of thionol (7-hydroxy-3*H*-phenothiazin-3-one) (**I**) in HCl is converted into the colourless leuco form (3,7-dihydroxy-3*H*-phenothiazin-3-one) by means of several strong reducing agents. This property was used for the detection of Sn^{2+}, Ti^{3+} and Cr^{2+}. The following sensitivities were attained—(*i*) in a test-tube: Sn^{2+} (pD 5·0), Ti^{3+} (pD 5·0) and Cr^{2+} (pD 6·0); (*ii*) on filter-paper: Sn^{2+} (pD 4·8), Ti^{3+} (pD 6·4) and Cr^{2+} (pD 6·3). For the detection, a 10^{-4}M soln. of **I** in 96% ethanol was used. Oxidising agents, V^{5+}, Fe^{3+} and I^- interfere. After conversion into $[Sn(OH)_3]^-$ in NaOH soln., Sn^{2+} can be detected in the presence of Cr^{2+} and Ti^{3+}. The quantitative course of the reactions was studied potentiometrically and a volumetric method was developed for the determination of Sn^{2+}, Cr^{2+} and Ti^{3+} with the use of 10^{-2}M-**I** soln. in 96% ethanol, at 50° to 60°, in conc. HCl in an atmosphere of CO_2; citric acid was added for the titration of Ti^{3+} to prevent hydrolysis. Bivalent Ni, Co^{2+}, Mn^{2+}, Zn^{2+} and Al^{3+} do not interfere, but Fe^{2+}, V^{5+} and, when determining Cr^{2+}, Sb^{3+}, must be absent. The mixture of Sn^{2+}, Cr^{2+} and Ti^{3+} can be potentiometrically differentiated and determined with an accuracy within ±1%. J. ZÝKA

418. **New Nessler reagent and its use in the direct nesslerisation of Kjeldahl digests.** K. R. Middleton (Rubber Res. Inst. of Malaya, P.O. Box 150, Kuala Lumpur). *J. Appl. Chem.*, 1960, **10** (7), 281–286.—For nitrogen in plant material, the procedure recommended is comparable in accuracy to a distillation - titration method. The new reagent (prepared by dissolving 9 g of HgI_2 and 12 g of KI in 1 litre of water) (soln. *A*) is stable and is used in conjunction with gum acacia to prevent flocculation of the colour complex. To 10 ml of test soln. (containing 2 to 3 p.p.m. of ammoniacal N) add the protective colloid (1 g of gum acacia dispersed in 50 ml of cold water, to which are added 1 ml of soln. *A* and 5 ml of N-NaOH; this is set aside overnight, then filtered through glass wool, and made up to 500 ml) (5 ml) and soln. *A* (5 ml). Mix thoroughly, then add N-NaOH (10 ml), mix again, and after 30 min. measure the extinction at 430 mμ in a 4-cm cell. A blank determination is necessary. The amount of N is read from calibration curves. Many interferences have been eliminated, but Ca, Mg, Cu, Mn, Fe and Cr interfere. Mercury, I^-, S^{2-}, alcohols, aldehydes and ketones must be absent. The sensitivity is 5 μg and the coefficient of variation is 1·4%. R. M. S. HALL

419. **The use of mercurated phenolphthalein and fluorescein in chemical analysis.** M. Wroński (Inst. f. Chem. Technol., Univ. Łódź, Poland). *Z. anal. Chem.*, 1960, **175** (6), 432–436 (in German).—Mercury in mercurated fluorescein or phenolphthalein is determined directly (in fluorescein only), or after release of Hg^{2+} by adding Br, by titration with thioglycollic acid, with thiofluorescein as indicator. The colour change from red to blue which occurs on adding certain compounds to mercurated phenolphthalein in dil. NaOH, and the further changes which occur on adding CN^- and thiourea, can be used as qualitative tests for S^{2-}, methanethiol, cysteine, CN^-, $S_2O_3^{2-}$, I^-, cyanuric acid, albumin, mercaptobenzothiazole, xanthate, diethyldithiocarbamate and thiourea. Compounds containing –SH, –NH·CS– or repeated –NH·CO– groups, I^- or CN^- quench the fluorescence of mercurated fluorescein; the extent of the quenching can be used for distinguishing a number of such compounds. The quenching also affords a very sensitive method for the determination of a number of compounds, including H_2S (0·02 μg), thiourea (0·04 μg), CS_2 (0·02 μg) and gelatin (2 μg). R. M. ROWLEY

420. **New scheme of analysis for the common anions based on paper chromatography.** I. I. M. Elbeih and M. A. Abou-Elnaga (Fac. Sci., Univ. Cairo, Egypt). *Anal. Chim. Acta*, 1960, **23** (1), 30–35.—Twenty-four common anions are separated on paper strips by a solvent mixture of ethanol - pyridine - H_2O - conc. aq. NH_3 (15:5:4:1). For each complete analysis 12 strips are required. The chromatograms are sprayed with a soln. of 1-naphthylamine-5-sulphonic acid, ammoniacal $AgNO_3$ and fluorescein for location and tentative identification of the spots. Confirmatory tests are then applied by spraying with more selective reagents. H. N. S.

421. **Localisation of spot-test colours by use of the ring-oven.** H. Weisz and P. W. West (Coates Chem. Lab., Univ., Baton Rouge, La., U.S.A.). *Mikrochim. Acta*, 1960, (4), 584–585 (in English).—Test stains that might otherwise diffuse widely on paper can be concentrated by use of a ring-oven. The sensitivity of the test is thus increased, generally by a factor of 10 to 100. Tests mentioned are for Fe^{III} with SCN^-, for CrO_4^{2-} with diphenylcarbazide, for Ti with H_2O_2, and for H_3BO_3 with turmeric soln. The sample is washed from the centre with 0·1N-HCl to meet the reagent applied as a ring at a distance from the centre. J. P. STERN

422. **Analytical possibilities of low-boiling-point organic solvent vapours in the spot-analysis technique.** F. Feigl, D. Goldstein and D. Haguenauer-Castro (Lab. da Prod. Mineral, Min. da Agric., Rio de Janeiro, Brazil). *Rec. Trav. Chim. Pays-Bas*, 1960, **79** (6), 531–540 (in German).—The uses of pyrolytic reactions of low-boiling-point solvent vapours in conjunction with spot analysis, with particular reference to $CHCl_3$, CCl_4 and CS_2 reactions, are discussed. Higher oxides of Cu, W and Cr may be used in the pyrolytic oxidation at 240° of $CHCl_3$ and CCl_4 to give Cl, which is tested for on a paper impregnated with a benzene soln. of thio-Michler ketone. Pyrolytic reduction of $CHCl_3$ or CCl_4 with benzoin at 220° produces HCl, which may be detected with Congo red indicator paper. Manganese sulphate hydrate is used for pyrolytic hydrolysis at 240° of $CHCl_3$ and CCl_4 to produce HCl; similarly CS_2 at 270° gives H_2S. Pyrolytic reaction with ammonia produced from guanidine carbonate at 190° and dissociation of CCl_4 and $CHCl_3$ in the presence of the oxides of Th, Zr, Ti and Nb to form Cl are other reactions described. Whilst the quant. nature of these reactions has not been substantiated, they are suitable for distinguishing between $CHCl_3$ and CCl_4. G. P. MITCHELL

423. **A screened indicator of methyl orange with sulphonated copper phthalocyanine.** T. P. Sastry and S. A. Pratt, III (Texas Southern Univ., Houston, U.S.A.). *Z. anal. Chem.*, 1960, **175** (3), 182–186 (in English).—The use of (87·3% pure) copper phthalocyanine-4,4′,4″,4‴-tetrasulphonate (potassium salt) as a 1:1 mixture with methyl orange narrows the pH range for colour change to between pH 3·3 and 3·6 and gives excellent colour contrast. A 1:4 mixture that changes colour between pH 3·6 and 4·0, however, is more useful as a substitute for methyl orange. The mixture is stable and of use for titrations of 0·1N soln., even in artificial light.
J. P. STERN

424. **Use of chelatochrome indicators in precipitation titrations. I.** R. Püschel and E. Lassner (Inst. Med. Chem., Univ., Graz, Austria). *Chemist Analyst*, 1960, **49** (2), 58–62.—A chelatochrome indicator is defined as an organic compound that forms coloured chelates with a metal ion and thereby serves for the detection of the end-point in a titration involving that metal. The conditions essential for the use of such indicators are defined, and their application to the determination of phosphate, arsenate and vanadate is described. (39 references.)

II; III. R. Püschel and E. Lassner. *Ibid.*, 1960, **49** (3), 90–94; 1960, **49** (4), 120–124.—A review and bibliography containing 265 references are presented.
N. E.

425. **A primary standard for alkalimetry and chelatometry.** J. E. Powell, J. S. Fritz and D. B. James (Dept. of Chem., Iowa State Univ., Ames, U.S.A.). *Anal. Chem.*, 1960, **32** (8), 954–957.—Cadmium *N*-hydroxyethyl(ethylenediamine)-*NN′N′*-triacetate has been shown to be an excellent reagent for the standardisation of bases and chelating agents such as EDTA. It is easily prepared and purified and is virtually non-hygroscopic and completely stable.
K. A. PROCTOR

426. **The determination of end-points in iodimetry [with starch].** L. Erdey and L. Pólos (Inst. of Gen. Chem., Polytech. Univ., Budapest, Hungary). *Period. Polytech.*, 1960, **4** (2), 157–162 (in German).—The end-point in the titration of iodine with thiosulphate is improved by using an aq. soln. of an amylose starch fraction as indicator, and by limiting the KI concn. at the end-point to $< 0{\cdot}1$M.
J. W. PRICE

427. **Oxidation with manganate solutions. III. Reduction of manganate with hydrogen peroxide and bivalent manganese.** I. M. Issa and M. G. E. Allam (Fac. of Sci., Cairo Univ., Egypt). *Z. anal. Chem.*, 1960, **175** (2), 103–110 (in English).—The titration of manganate with H_2O_2 and Mn^{2+} soln. is based on the reactions—

(*i*) $MnO_4^{2-} + H_2O_2 \rightarrow MnO_2 + 2OH^- + O_2$ and
(*ii*) $MnO_4^{2-} + Mn(OH)_2 \rightarrow 2MnO_2 + 2OH^-$.

These titrations are discussed. Provided that telluric acid is present in a sufficient quantity (ratio of Mn^{2+} to Te^{6+} is 1:4) in the first reaction medium and the soln. is 1 to 2N in NaOH accurate results are obtained. The errors under these conditions vary from $+0{\cdot}37\%$ to $-0{\cdot}75\%$. The second reaction is less rapid and the ratio of MnO_4^{2-} to Te^{6+} should be $\ll 1:15$ and the soln. $< 0{\cdot}04$M in NaOH in order to obtain good results. Some titration curves are shown.
B. B. BAUMINGER

428. **The use of potassium manganate in quantitative analysis. V. The stability of potassium manganate solutions at higher temperatures.** H. L. Polak and G. den Boef (Lab. f. Anal. Chem., Univ., Amsterdam, Holland). *Z. anal. Chem.*, 1960, **175** (4), 265–272 (in German).—The stability, with respect to the formation of Mn^{2+}, of 0·03 and 0·004M-K_2MnO_4 in 1 and 3M-KOH is examined in the temp. range 60° to 100° and also in the presence of H_2TeO_4 and MnO_2. At 60° there is no loss of stability for 4 hr. and the loss over 12 hr. is $< 0{\cdot}5\%$. Losses increase at higher temp. Thus K_2MnO_4 is a very useful quant. reagent for the oxidation of both inorganic (*e.g.*, S^{2-}, CN^- and SCN^-) and organic substances (*e.g.*, formic, glycollic and mandelic acids) in alkaline media. The rate of reaction at 60° is satisfactory.
J. P. STERN

429. **Oxalate interference in cerimetry.** L. J. Csányi and F. Szőke (Inst. f. Inorg. and Anal. Chem., Univ. of Szeged, Hungary). *Z. anal. Chem.*, 1960, **175** (3), 187–195 (in English).—The positive error caused by oxalic acid in the titration with $Ce(SO_4)_2$ of, *e.g.*, Fe^{2+}, quinol or indigo carmine, is ascribed to the competing reaction between oxalate ions and Ce^{IV}. The stability of the Ce^{IV}-oxalate complex is somewhat greater than that of trisulphatocerate. The error is reduced by increasing the H_2SO_4 concn. and by adding H_3PO_4, F^- or Cl^- in sufficient amount, since all these reduce the rate of the reaction of Ce^{IV} with oxalate.
J. P. STERN

430. **Ethylenediaminetetra-acetic acid in volumetric analysis. Determination of metals.** O. Borchert (Schönebeck, Elbe, Germany). *Chem. Tech., Berlin*, 1960, **12** (6), 332–342.—A review, with 121 references.

431. **EDTA titrations employing "SNAZOXS" as the indicator.** G. Guerrin, M. V. Sheldon and C. N. Reilley (Dept. of Chem., Univ. of N. Carolina, Chapel Hill, U.S.A.). *Chemist Analyst*, 1960, **49** (2), 36–38.—Procedures are given for the titration of Bi, In, Pb, Fe, Cu, Zn, Co, Ni, Cd, La, Hg, Al and Ga with EDTA, with a saturated soln. of SNAZOXS [8-hydroxy-7-(4-sulpho-1-naphthylazo)quinoline-5-sulphonic acid] in dimethylformamide as indicator. For direct titrations the colour change is from yellow to orange or pink. Back-titrations are made with Cu^{2+} soln. In some direct titrations Cu^{2+} soln. is added to sharpen the end-point. Iron and Al can be determined in the presence of each other.
G. BURGER

432. **Potentiometric titrations in trimethylamine-glacial acetic acid solution.** W. Hubicki and R. Wiącek (Inst. of Inorg. Chem., Curie-Skłodowska Univ., Lublin, Poland). *Z. anal. Chem.*, 1960, **175** (2), 97–103 (in German).—The application of trimethylamine in glacial acetic acid as solvent in the potentiometric titration of a variety of compounds, *e.g.*, Tl acetate with KI, $SnCl_2$ with $K_2Cr_2O_7$, hydrazine sulphate with KIO_4, and $AgNO_3$ with NH_4Cl, has been studied. Its preparation and physical and chemical characteristics are discussed.
B. B. BAUMINGER

433. **Current and titration efficiencies of electrically generated manganic ion. Ferric-manganous sulphate dual intermediate system.** A. J. Fenton, jun., and N. H. Furman (Univ., Princeton, N.J., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 748–752.—Optimum conditions for the anodic generation of

Mn^{3+} by electrolytic oxidation of Mn^{2+} at a platinum or gold anode are reported and discussed in respect of acidity, c.d. and concn. of Mn^{3+}. Max. current efficiency (> 99·5%) is attained by direct oxidation of Mn^{2+} to Mn^{3+} in 0·3M-$MnSO_4$ - 0·1N-$Fe_2(SO_4)_3$ - 4N-H_2SO_4 - 4%H_3PO_4 at a platinum anode with a generating current of 10 to 20 mA and a c.d. of <1·5 mA per sq. cm. Either Mn^{3+} or Fe^{2+} can be generated first without affecting the precision or accuracy of the results for titration efficiency, which are quant. if a reductant is present.

W. J. BAKER

434. **Neutron activation analysis as an analytical tool.** D. Mapper (Anal. Chem. Branch, A.E.R.E., Harwell, Berks., England). *Chimia*, 1960, **14** (7), 241–248 (in English).—A review of the technique and applications of neutron activation analysis is presented. Sources of error and the limitations of the method are discussed. N. E.

435. **Reports on analytical methods.** U.K.A.E.A. (Production Group, Operations Branch, Windscale, Cumberland). The following reports have been issued by the U.K.A.E.A., Risley, Warrington, Lancs. **Polarographic determination of cadmium in nitric acid solutions of uranyl nitrate,** PG Report 125(W), 7 pp. **Determination of uranium in uranyl nitrate solutions (ceric sulphate titration),** PG Report 126(W), 5 pp. **Polarographic determination of copper in uranium solutions,** PG Report 139(W), 5 pp.

See also Abstract—**771**, Determination of substances in solution.

2—INORGANIC ANALYSIS

General, determination of elements (arranged in the order of the Periodic Table), analysis of minerals and inorganic industrial products.

436. **Trace monitoring in gases using galvanic systems.** P. A. Hersch (Arthur D. Little Res. Inst., Inveresk, Midlothian, Scotland). *Anal. Chem.*, 1960, **32** (8), 1030–1034.—A galvanic system is described for the determination of oxygen in trace amounts in gases, body fluids, photosynthesis studies and tumour irradiation, and for the indirect measurement of hydrogen and other combustible gases. The conventional carbon cathode is replaced by silver and the zinc anode by a base metal. If the silver cathode is not completely immersed in the soln. the sensitivity is greatly increased.

K. A. PROCTOR

437. **Precipitation of metals with aliphatic arsonic acids.** R. Pietsch (Inst. f. anal. Chem., Univ., Graz, Austria). *Mikrochim. Acta*, 1960, (4), 539–552 (in German).—Ethyl- (**I**), n-propyl- (**II**), and n-butyl-arsonic acid (**III**) are used to precipitate metals. Thus **I** gives cryst. ppt. with Ca, La, Ce, Cu, Zn, Cd, Hg^{2+}, Pb and Bi, flocculent ppt. with Y, Ti, Zr, Th, Mn^{2+} and Sn^{2+}, and coloured ppt. with Fe^{3+} (greenish), Co^{2+} (violet), and UO_2^{2+}, Ni^{2+}, Cu^{2+} and Ag (yellowish). **II** gives cryst. ppt. with Ca, La, Cd, Hg^{2+}, Pb and Bi, flocculent ppt. with Al, Y, Ce^{3+}, Ti, Zr, Th, Mn^{2+}, Ni, Cu, Zn, In, Sn^{4+} (slimy) and Sn^{2+}, and coloured ppt. with UO_2^{2+}, Fe^{2+}, Fe^{3+}, Ag and Co^{2+}. **III** gives cryst. ppt. with Mg, Ca, Cd and Hg, flocculent ppt. with Be, Al, Y, La, Ce^{3+}, Ti, Zr, Th, Mn^{2+}, Cu, Zn, In, Sn, Bi and Pb, and coloured ppt. with Cr^{3+}, UO_2^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Ag. The pH for incipient pptn. is given and the quant. or non-quant. nature of the pptn. is noted. Passage from H_3AsO_4 to methylarsonic acid and to **I** shifts the pH for incipient pptn. to higher values, so that some metals, *e.g.*, Fe^{3+}, Cr^{3+} and Al, are not pptd. and others only partially; this is of use for preventing pptn. of metals by OH^-. With **II** and **III** these pH values drop again, and prevention of pptn. becomes impossible. The light absorption of the ppt. is discussed. These acids can be used for the gravimetric or potentiometric determination of many metals. J. P. STERN

438. **Ion-exchange separation of metal cations.** J. S. Fritz and S. K. Karraker (Inst. for Atomic Research, Iowa State Univ., Ames, U.S.A.). *Anal. Chem.*, 1960, **32** (8), 957–960.—The rate of elution of 24 bi-, ter- and quadri-valent cations from Dowex 50-X8 or 50W-X8 (ethylenediammonium form) with ethylenediammonium perchlorate soln. (0·1M and 0·5M) is reported. Results of the application of the procedure to 33 pairs of cations are given.

T. R. ANDREW

439. **Coulometric titration of noble metals with monothio ethylene glycol [2-mercaptoethanol].** B. Miller and D. N. Hume (Dept. Chem. and Lab. Nucl. Sci., Mass. Inst. Technol., Cambridge, U.S.A.). *Anal. Chem.*, 1960, **32** (7), 764–767.—Coulometric generation of SH^- from the Hg^{2+} complex of 2-mercaptoethanol (**I**) is possible at const. current without serious interference from secondary complexes involving the hydroxyl group. The coulometric titration of 0·1 to 3 mg of Hg^{2+}, Au^{3+}, Ag^+, Pd^{2+}, Pt^{2+} and Cu^{2+} with electrolytically generated **I** at pH 4·6 to a pre-set potentiometric end-point is therefore practicable, and is more sensitive than is the thioglycollic acid method for Au and Hg (*Ibid.*, 1960, **32**, 524). For Cu^{2+} and Pt^{2+}, back-titration of a slight excess of SH^- is recommended; Pd^{2+} can be titrated in the presence of Rh^{3+} because this ion gives no potentiometric response. The generating current is 5 to 10 amp. and the c.d. ≃ 1·5 mA per sq. cm. The error is usually within ± 1%. The application of the method, with modification, to the coulometric titration of $Fe(CN)_6^{4-}$ is discussed. W. J. BAKER

440. **Studies of absorption spectra of some 2,2′-dipyridyl and 1,10-phenanthroline metal complexes.** J. Császár (Inst. for Gen. and Phys.-Chem. Sci., Univ. Szeged, Hungary). *Magyar Kém. Foly.*, 1960, **66** (7), 267–271.—The i.r. absorption spectra of the complexes of Fe^{II}, Fe^{III}, Co^{III}, Co^{II}, Rh^{III}, Rh^{I}, Cu^{II} and Cu^{I} with 2,2′-dipyridyl and 1,10-phenanthroline were measured by means of a Beckman DU spectrophotometer. The mechanism of the light absorption is discussed and spectra of iso-electronic metal complexes are compared. The results obtained are compared with those published in the literature. (40 references.) B. VASZKO

441. **Absorption spectra of molten fluoride salts. Solutions of several metal ions in molten lithium fluoride - sodium fluoride - potassium fluoride.** J. P. Young and J. C. White (Anal. Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 799–802.—Spectra have been obtained for the fluorides of Ni, Co, Cr and Pr, and for UF_4, dissolved in molten LiF - NaF - KF eutectic at temp. between 500° and 650°, and these spectra are compared with those obtained in other molten salts and in aq. soln. The methods of preparing

the fluoride melt and of obtaining the spectra in the high-temp. cell assembly of Young and White (*Ibid.*, 1959, **31**, 1892) are described.

K. A. PROCTOR

442. **Separation and determination of argon, oxygen and nitrogen by gas chromatography.** E. W. Lard and R. C. Horn (W. R. Grace & Co., Memphis, Tenn., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 878–879.—By passing a 10-ml sample of the gas mixture through a column (6 ft. × 0·25 in.) of activated Linde Mol. Sieve 5 A, first at 25° and then at −72°, with a He flow of 100 ml per min., two chromatograms are obtained. The first shows a separation of N from Ar plus O, and the second a separation of Ar from O, N being retained on the column. The concn. of each component is calculated from peak areas by using the relative response factors reported by Messner *et al.* (*Ibid.*, 1959, **31**, 230). The Mol. Sieve (30 to 70 mesh) must be activated by oven-drying at 300° for 1 hr. and then immediately transferred to the column, through which a small flow of He is passed until the temp. reaches 25°. The method is sensitive to 20 p.p.m.

W. J. BAKER

443. **Paper-chromatographic separation of silver, lead and mercurous mercury.** V. K. Mohan Rao (Central Drug Res. Inst., Lucknow, U.P.). *J. Sci. Ind. Res., B, India*, 1960, **19** (5), 171–173.—Paper chromatography of Ag^+, Pb^{2+} and Hg_2^{2+} as nitrates on Whatman No. 1 paper is effected with 0·2N-aq. H_2SO_4 and with a satd. soln. of NH_4NO_3, diluted 80 times and mixed with aq. NH_3 (5:2). The separation obtained is illustrated. The separation of Pb^{2+} and Ag^+ with 0·3N-aq. NH_3 allows a rough quant. estimation to be made.

E. J. H. BIRCH

444. **Rapid method for determining alkali and alkaline-earth elements with an ion exchanger.** Hiroyuki Tsubota and Yasushi Kitano (Nat. Inst. Radiolog. Sci., Kurosuna-macho, Chiba). *Bull. Chem. Soc. Japan*, 1960, **33** (6), 770–775.—Alkali and alkaline-earth elements and the rare elements are separately eluted easily, rapidly and completely from Dowex 50 or Amberlite IR-120 (H^+ form) by a buffer soln. of M-formic acid and M-ammonium formate.

I. JONES

445. **Spectrochemical determination of lithium, sodium, potassium and rubidium in rocks and minerals using the Stallwood jet.** D. M. Shaw, O. C. Wickremasinghe and J. N. Weber (McMaster Univ., Hamilton, Canada). *Anal. Chim. Acta*, 1960, **22** (4), 398–400.—The samples are mixed with graphite and Cs_2CO_3, and Cs serves as an internal standard. Spectral lines and precision data are tabulated. The Stallwood jet has been described elsewhere (*cf. Anal. Abstr.*, 1954, **1**, 1736).

H. N. S.

446. **Acidimetric micro-determination of sodium after precipitation as sodium zinc uranyl acetate.** D. Ceauşescu (Inst. for Hygiene, Timişoara, Romania). *Z. anal. Chem.*, 1960, **176** (1), 1–3.—The triple acetate is dissolved in water and passed through an ion-exchange column in the acid form. All the cation exchanges quant., and the acetic acid in the percolate is titrated with alkali. *Procedure*—The pptn. of the Na^+ (0·1 to 1 mg) is carried out in a centrifuge tube by the normal procedure. The ppt. is washed four or five times with acetone or ethanol satd. with triple acetate, and two or three times with ethyl ether. After removal of ether, the ppt. is dissolved in water and transferred to an ion-exchange column (12 mm diam.) containing 10 ml of Wofatit F in the acid form. The soln. and the first 5 to 10 ml of the wash water are allowed to pass through at a rate of 1 drop per sec. and the remaining 20 to 75 ml of wash water at 2 drops per sec. The percolate is titrated with 0·02N-NaOH in the presence of phenolphthalein to the first appearance of the red colour; CO_2-free air is drawn through the titration flask. The results are accurate to within 2%.

J. H. WATON

447. **Determination of potassium by precipitation with sodium cobaltinitrite.** G. K. Chaturvedi and Abani K. Bhattacharya (Agra College, India). *Z. anal. Chem.*, 1960, **175** (6), 401–404 (in English).—Freshly prepared sodium cobaltinitrite was added to K_2SO_4 and KCl soln., and the ppt. was dried at 110° and weighed as $K_2Na[Co(NO_2)_6].H_2O$. Soln. containing nitric acid gave low results, as did soln. containing no acid. The weight of ppt. obtained from soln. containing ethanol varied with the ethanol concn. and the time of standing before filtration, and errors varying between +3·5% and −9·0% were observed. The best results were obtained when the soln. contained 5 ml of 40% (v/v) ethanol in a total volume of 35 ml, and the ppt. was washed with 40% ethanol. The error was then ≃ − 0·5%, and was only slightly affected by time of standing before filtration.

R. M. ROWLEY

448. **The complexometric determination of potassium.** M. Pećar (Med.-Chem. Inst., Univ., Graz, Austria). *Mikrochim. Acta*, 1960, (4), 567–576 (in German).—The interference of NH_4^+ in the determination of K^+ by the method of Flaschka and Holasek (*Anal. Abstr.*, 1958, **5**, 1942) is obviated by oxidation with NaOBr, excess of Br being reduced by formic acid. The use of commercial NaOH involves high blanks because of the appreciable K content. Trichloroacetic acid does not interfere.

J. P. STERN

449. **Chromatographic separation of francium from aesium and rubidium.** A. K. Lavrukhina, A. A. Pozdnyakov, S. S. Rodin and L. P. Moskaleva. *Dokl. Akad. Nauk SSSR*, 1960, **130** (1), 88–89; *Ref. Zhur., Khim.*, 1960, (14), Abstr. No. 56,671.—The method is based on the different distribution coeff. of Fr, Cs and Rb between the cationite KU-1 (H^+ form) and dil. HCl. As the HCl concn. increases to 5 to 6M, the distribution coeff. are greatly reduced, but remain constant in more concentrated acid. The greatest difference in distribution coeff. for pairs of neighbouring elements occurs when they are adsorbed from a soln. 5 to 6M or about 0·7M in HCl; under these conditions the coeff. for Fr and Cs are 2 and 3, respectively. To separate the elements, 0·05 to 0·1 ml of the HCl soln. is introduced into a column (13 cm × 0·3 cm) filled with the cationite (200 to 250 mesh) previously washed with dil. HCl. In all operations, including elution, acid of the same concn. is used. With 5·5M-HCl the three-component mixture is separated in 30 to 50 min. With 0·7M-HCl an effective separation of Cs and Rb is also obtained, but the process takes 4 to 5 hr. Francium cannot be separated from Cs in HCl soln. on resin KU-2.

C. D. KOPKIN

450. **3-Hydroxyiminomethylsalicylic acid as an analytical reagent. I. Gravimetric estimation of copper and nickel.** Asit Kumar Ray and Priyadaranjan Rây (Inorg. Chem. Dept., Indian Ass.

for the Cult. of Sci., Calcutta). *J. Indian Chem. Soc.*, 1960, **37** (3), 133–140.—The reactions of 3-hydroxyiminomethylsalicylic acid (**I**) with metal ions are studied. **I** behaves like salicylaldoxime with respect to colour, solubility, etc., of its metal derivatives, but the pH values of incipient pptn. of the metal ions are somewhat different. **I** also produces an orange-yellow ppt. with Ti in acid soln. (*cf.* Flagg and Furman, *Ind. Eng. Chem., Anal. Ed.*, 1940, **12**, 529). Soluble coloured complexes are given by Fe^{3+} and U^{4+} in acid and alkaline medium, respectively. The use of **I** for the gravimetric determination of Cu and Ni, which furnish ppt. of the composition $M(C_9H_6O_2N)_2$, ($M = Cu^{2+}$ or Ni^{2+}), after drying at 110°, is described. Copper is separated from Hg^{2+}, Pb^{2+}, Al^{3+}, Cd^{2+}, Zn^{2+}, Mn^{2+} and Co^{2+} by pptg. with an excess of **I** at pH 2·5 to 3·0; for its separation from Fe^{3+}, Sb^{3+} and Bi^{3+}, the pptn. has to be carried out at pH 2·5 to 3·0 in the presence of tartaric acid. Arsenite, arsenate, vanadate and phosphate do not interfere at pH 2·5 to 3·0. Bivalent Ni is determined at pH 5·6 to 6·0. I. JONES

451. **Determination of low selenium contents in copper as piazselenole [benzo-2,1,3-selenadiazole] after dry separation.** W. Gebauhr and A. Spang (Siemens-Schuckertwerke A.-G., Erlangen, Germany). *Z. anal. Chem.*, 1960, **175** (3), 175–181 (in German).—The Se in copper filings volatilises at 1000° in a slow stream of O as SeO_2; the loss, determined by the use of ^{75}Se, averages 1·5 and 3% for Se contents of 0·05 and 0·0002%, respectively. The SeO_2 sublimate is determined colorimetrically with 3,3′-diaminobenzidine (**I**). Over-all errors are $< \pm 5\%$ for 3 to 10 μg of Se. A 5-fold excess of Bi causes positive errors. *Procedure*—Heat the finely divided (144 mesh per sq. cm) copper sample (300 to 500 mg) in a sublimation apparatus at 1000° in a stream of O (8 to 10 ml per min.) for 60 min. Dissolve the sublimate in 0·2N-HCl (4 ml), add 0·5% **I** soln. in 0·1N-HCl (2 ml) and a soln. (2 ml) containing 1% of ammonium oxalate and 0·5% of NaF. Dilute to 10 ml and measure the extinction (2-cm cell) at 350 mμ after 30 min. J. P. STERN

452. **Micro-determination of silver and copper in silver-copper alloys using precision null-point potentiometry.** H. V. Malmstadt, T. P. Hadjiioannou and H. L. Pardue (Dept. of Chem. and Chem. Engng, Univ. of Illinois, Urbana, U.S.A.). *Anal. Chem.*, 1960, **32** (8), 1039–1041.—The method described can be used to determine Cu (by titration with iodine) at concn. of 20 to 100 p.p.m. with an average error of about 0·1 p.p.m. and a relative average deviation of 0·1%, and Ag (by titration with Cl^-) at concn. between 0·3 and 4·5 p.p.m. with a precision and accuracy better than 0·005 p.p.m. (*Cf. Anal. Abstr.*, 1961, **8**, 891.) K. A. PROCTOR

453. **Effects of temperature and non-aqueous solvent changes on silver dithizonate extractions.** F. F. Dyer and G. K. Schweitzer (Univ. of Tennessee, Knoxville, U.S.A.). *Anal. Chim. Acta*, 1960, **23** (1), 1–5.—Silver is extracted from M-$HClO_4$ into soln. of dithizone in $CHCl_3$ and CCl_4 at various temp. For each organic solvent the log of the extraction const. and the reciprocal of the absolute temp. are in linear relationship. When Ag^+ are extracted from 0·1M-KBr into soln. of dithizone in dichloromethane, $CHCl_3$, CCl_4, benzene or chlorobenzene a linear relationship is found between the extraction const. and the ratio of the solubilities of Ag dithizonate and dithizone in each organic solvent. H. N. S.

454. **Decomposition of ferrocyanide in analysis. III. Photometric ultra-micro determination of silver.** I. Kraljić (Tech. Fac., Univ., Zagreb, Yugoslavia). *Mikrochim. Acta*, 1960, (4), 586–591 (in German).—Silver catalyses the decomposition of $Fe(CN)_6^{4-}$ and makes Fe^{2+} available for complexing with 2,2′-dipyridyl. The extinction of this complex at 522 mμ is used to determine Ag. At pH 3·2 and at 65° the sensitivity is 0·001 μg per drop. The accuracy for 2×10^{-7} moles of $AgNO_3$ per litre is within ± 8%. J. P. STERN

455. **Photometric determination of silver as colloidal silver sulphide in the non-aqueous phase.** M. Ziegler and H. Sbrzesny (Anorg. Chem. Inst., Univ. Göttingen, W. Germany). *Z. anal. Chem.*, 1960, **175** (5), 321–324.—The trace-silver content of impure lead samples is determined by means of tri-n-butylammonium saccharin (**I**), which is prepared by mixing, in a separating-funnel, 175 ml of tri-n-butylammonium acetate with an aq. soln., of the max. possible concn., of 25 g of sodium saccharin. **I** forms the lower viscous layer and is run off and dissolved in dichloromethane (100 ml). *Procedure*—The lead sample (≯ 100 g), which may contain Bi, Cu, Fe, Co and Ni, in addition to Ag, is dissolved in HNO_3 (≃ 5N) (≯ 1 litre) and then buffered with ammonium acetate (solid or satd. soln.) to pH 4·5 to 5·0. An unspecified quantity of this soln. is treated with **I** soln. (1 ml) followed by dichloromethane (2 to 3 ml); dibromomethane or a mixture of the two solvents may be used to ensure that the non-aq. solvent forms the lower layer. After separation and a second washing of the aq. layer with 2 ml of dichloromethane the combined non-aq. extract is washed with 10 to 15 ml of H_2O containing **I** (1 ml) and the aq. layer is washed with fresh dichloromethane containing **I** (1 or 2 drops). The combined non-aq. extracts are mixed with 3 to 4 ml of collodion soln. (4%) (commercial 6% soln. diluted with ether) in a 20 to 25-ml measuring cylinder and diluted to vol. with methanol. One portion of this soln. is set aside as a blank while a second is treated with a stream of H_2S for 2 to 3 min., replacing any losses by evaporation. Photometric measurements between 320 and 350 mμ show that Beer's law is obeyed, even when samples are 24 hr. old, provided that both sample and blank are of the same age. Recoveries of 127 to 318 μg of Ag per 100 g of lead range from 97·5 to 100·9%. E. G. CUMMINS

456. **Non-destructive analysis of microgram quantities of silver by radioactivation.** Minoru Okada (Government Chem. Indust. Res. Inst., Shibuya-ku, Tokyo, Japan). *Nature*, 1960, **187**, 57–58.—A nuclear reactor JRR-1 and a RCL-256-channel pulse-height analyser are used. *Procedure*—The sample (0·1 to 10 g) is placed in the reactor for 30 sec., and irradiated at a flux of 3×10^{11} neutrons per sq. cm per sec., then cooled for 10 sec., counted for 20 sec., cooled for 10 sec., and counted for 20 sec. The scintillator used is a well-type NaI crystal, 2 in. thick. An aluminium vessel (2·5 mm thick) is inserted in the well to absorb β-rays. The resulting γ-spectrum shown on the monitor (Braun tube) is photographed and the height of the photopeak due to 0·66-MeV γ-rays with ^{110}Ag ($T_{\frac{1}{2}} = 24{\cdot}2$ sec.) is measured and compared with a standard treated in the same way. The limit of detection of Ag in zinc sulphide is ≃ 1 p.p.m. but,

with elements less activated than Zn, the detection limit is < 1 p.p.m. Interference by Pb is negligible, but Bi interferes slightly. R. A. HENDEY

457. **Separation of silver from cobalt and nickel by ion-exchange chromatography.** R. P. Bhatnager and R. P. Shukla (Dept. of Chem., Holkar Coll., Indore, India). *Anal. Chem.*, 1960, **32** (7), 777–778.—Both low and high concn. of Ag can be separated quant. from Ni and Co by passing the sample soln. through a column (50 cm × 1 cm) of Amberlite IR-120 (Na^+ form) at a flow rate of 8 ml per sq. cm per min. and then eluting the Ag^+ with 2% aq. $NaNO_3$. The Ag^+ in the eluate can then be titrated, without interference from coloured ions, by the modified Volhard method described. The error is within ± 0·5%, and the procedure is suitable for ores and alloys. W. J. BAKER

458. **Simplified method for the determination of gold for prospecting purposes.** V. Patrovský (Inst. Mineral Raw Materials, Prague). *Geologický Průzkum*, 1960, (2), 52–53.—*Procedure*—To the homogenised sample (10 to 25 g) add conc. HCl (10 to 25 ml), H_2O (2 to 5 ml) and Br (1 to 2 ml), and set aside for 15 min.; add a few drops of H_2O_2 and evaporate on a water bath to a syrup. Add conc. HCl (2 ml) and bromine water (1 ml) and heat; dilute with H_2O (30 ml), filter or centrifuge, wash the ppt. with H_2O and dilute the filtrate to 50 ot 100 ml. Evaporate the Br from an aliquot, add KBr (2 g for 50 ml) and a few drops of satd. salicylic acid soln., and shake. Extract with butyl acetate (15 ml), dry the extract with anhyd. Na_2SO_4 and measure the extinction at 400 mμ. For samples containing more than a 100-fold excess of Fe, add H_3PO_4, before the extraction, till the soln. becomes pale but not colourless. With samples containing more than a 1000-fold excess of Fe, shake the extract, after separation, with 25 ml of a soln. containing KBr (1 g), conc. HCl (1 ml) and conc. H_3PO_4 (0·25 ml). The procedure yields satisfactory results for samples containing as little as 0·002% of Au and 20% of Fe. Small amounts of V, W and Mo and large amounts of Cu do not interfere. J. ZÝKA

459. **Micro-determination of beryllium by fluorimetry of the morin - beryllium complex.** J. Bril and E. Pruvot (Co. Léchiney L.R.M., St-Jean-de-Maurienne, France). *Mikrochim. Acta*, 1960, (4), 577–579 (in French).—The fluorescent complex of Be with morin (**I**) has the composition Be_2I_2. The intensity of fluorescence is max. with incident light of 480 mμ and with NaOH concn. ≃ 0·1N, and increases with ethanol concn. up to ≃ 60%. The limit of detection is 5×10^{-4} μg of Be per ml. J. P. STERN

460. **Fluorimetric determination of beryllium in bronze with morin.** Z. Holzbecher and J. Pokorný (Dept. Anal. Chem., Inst. Chem. Technol., Prague). *Chem. Listy*, 1960, **54** (5), 470–473.—The addition of EDTA (disodium salt) permits the determination of Be in the presence of a 1000-fold excess of Cu, Ni, Co or Mg, a 100-fold excess of Fe and a 3-fold excess of Mn. *Procedure*—Dissolve the sample (0·5 g) in HNO_3 (1:1) (15 ml), remove oxides of N by boiling, then cool and filter; wash with hot 1% HNO_3, dilute the filtrate to 500 ml and dilute 50 ml of this soln. to 500 ml. To an aliquot (1 to 10 ml) of this soln. add 5% EDTA (disodium salt) soln. (10 ml) and 2N-NaOH (5 ml). Dilute to 80 ml with H_2O, add 0·02% ethanolic morin soln. (1 ml), dilute to 100 ml with H_2O and measure the fluorescence. Compare with a calibration curve. The method is suitable for the determination of 0·05 to 5% of Be with an accuracy of ± 5%. The time required is 10 to 15 min. J. ZÝKA

461. **Determination of oxygen in oxides of the calcium group.** H. Hartmann and G. Ströhl (Anorg.-Chem. Inst., Braunschweig, Germany). *Z. anal. Chem.*, 1960, **175** (2), 84–94 (in German).—A method described previously (Hartmann *et al.*, *Z. Erzbergb. Metallhüttenw.*, 1955, **8**, 18) has been extended to the direct determination of oxygen in CaO, SrO, BaO and MgO. It is based on the reaction—

$$MO + H_2S \rightleftharpoons MS + H_2O,$$

and the water formed is absorbed in a Friedrich absorption tube containing P_2O_5 and weighed. Detailed illustrations of the apparatus for the determination and preparation of pure oxides are given. The method fails for BeO. The mean error is ± 1%. B. B. BAUMINGER

462. **Ethylenedinitrilotetra-acetic acid titration of calcium in electrolytic baths in aluminium reduction cells.** A. D. Behel, sen., and J. Pendley (Listerhill Reduction Plant, Reynolds Metals Co., Sheffield, Ala., U.S.A.). *Anal. Chem.*, 1960, **32** (8), 1051.—The method described is a modification of the methods of Cheng (*Anal. Abstr.*, 1957, **4**, 348) and of Hildebrand and Reilley (*Anal. Abstr.*, 1957, **4**, 2518) and has been developed for use in routine control electrolytic bath analysis. It is as accurate and precise as the oxalate - permanganate titration and, in addition, the use of filter-paper, and the filtration and washing steps, which are required in the oxalate method, are eliminated. K. A. PROCTOR

463. **Flame-photometric determination of calcium in aluminium and in silumins.** Z. Kubišta, V. Kabický and N. Tietz (SVÚOM, Prague). *Hutn. Listy*, 1960, **15** (6), 479–480.—The sample (2 g, containing 0·05 to 2% of Ca) is dissolved in HCl, SiO_2 is filtered off and the Ca emission is measured directly with the flame photometer Zeiss Model III, with interference filter Ca 63. The calibration curve is prepared from soln. containing added pure Al or silumin. The emission decreases in the presence of Al and Si; the interference due to Al can be removed by using a higher temp. for the combustion mixture (acetylene - air) or by the addition of a strontium salt and the use of the interference filter Ca 54. Iron and Mn (≯ 1%) do not interfere. For alloys containing Cu and Zn a special calibration curve must be prepared. J. ZÝKA

464. **Use of ethylenediaminetetra-acetic acid in the separation of radioactive barium and strontium.** H. A. C. Montgomery (D.S.I.R., Water Pollution Res. Lab., Stevenage, Herts., England). *Analyst*, 1960, **85**, 524–526.—The method is designed for application to the ppt. of mixed nitrates customarily obtained from 75% HNO_3. The neutral or faintly acid soln. (≡ 10 mg each of Ba and Sr in 2 ml) is treated with a $La(NO_3)_3$ - EDTA reagent and K_2CrO_4 at 100°. The pptd. $BaCrO_4$, washed with NH_4NO_3 soln., is separated by centrifuging and reserved for purification. The combined supernatant liquid and washings are treated with $(NH_4)_2SO_4$ soln., $Ca(NO_3)_2$ soln. and $BaCl_2$ soln. and, after a period at 100°, the cooled liquid is centrifuged and the ppt. is washed with NH_4NO_3 soln. and discarded. The supernatant liquid and washings are treated with aq. NH_3, $(NH_4)_2SO_4$ soln. and $CuSO_4$ soln. at 90°.

After 10 min. at 90° the liquid is centrifuged, the ppt. of $SrSO_4$ is washed with water, and the supernatant liquid and washings are discarded. The ppt. is dissolved in EDTA soln., NH_3 is expelled by heating to 100°, and $(NH_4)_2SO_4$ soln. and an ammonium acetate buffer soln. (pH 5·0 ± 0·1) are added. After being heated for 5 min. the liquid is cooled and centrifuged and the ppt. is washed with 2N-aq. NH_3 and water, weighed and counted. The $BaCrO_4$ ppt. (*supra*) is dissolved in 2N-HNO_3, EDTA soln. is added and K_2CrO_4 at 100°. The ppt. is washed with aq. NH_3 and water, weighed and counted immediately. A. O. JONES

465. **Electrolytic and electrochemical separation of radium-D, radium-E and polonium from ethylenediaminetetra-acetate solution.** V. Vebersík (Fachsch. f. Kerntechnik, Prague, Czechoslovakia). *Z. anal. Chem.*, 1960, **175** (6), 405–415 (in German).—Radium-D (^{210}Pb) plus radium-E (^{210}Bi) and Po were separated by electrolysis from the very dilute soln. in EDTA soln. obtained when Ra is separated from its decay products (*cf.* Vebersík and Horová, *Anal. Abstr.*, 1959, **6**, 1645). The optimum conditions for the isolation of ^{210}Pb plus ^{210}Bi by electrolysis were found to be—nickel cathode and platinum anode, each 10 mm × 10 mm × 0·2 mm; temp. 80°; pH 3·5 (HNO_3); 3·5 V; time 2·5 hr.; stirring speed 5 rev. per sec.; ^{210}Pb concn. equiv. to 200 μC in 50 ml. The deposit on the anode contained 77·5% of the ^{210}Bi and 95% of the ^{210}Pb initially present in the soln. For the isolation of Po by internal electrolysis the best conditions were—silver electrode (10 mm × 10 mm × 0·2 mm); temp. 90°; pH 3 (HCl); time 2 hr.; stirring speed 15 rev. per sec.; Po concn. equiv. to 1000 μC in 5 ml; 98% of the Po was recovered. R. M. ROWLEY

466. **Determination of metal ions in solution by means of TAA [thioacetamide] and EDTA. I. General introduction and determination of zinc.** G. C. Krijn and G. den Boef (Univ. Amsterdam, Netherlands). *Anal. Chim. Acta*, 1960, **23** (1), 35–41.—Methods are described for the determination of Zn when metals of groups 2 and 3 are present. Tin is first removed as $SnO_2.nH_2O$ after treatment with HNO_3. Lead is separated as $PbSO_4$ either before the Zn is pptd. or after the ZnS is re-dissolved. *Procedure*—To 5 ml of a slightly acid soln., containing 0·6 to 6 mg of Zn, add 1 ml of 4N-HCl and 1 ml of 2 or 6% thioacetamide soln. Heat at 90° for 20 min., centrifuge, remove the liquid with a G4 filter-stick and wash the ppt. with water (3 × 1 ml). Concentrate the filtrate to 5 ml, add a few drops of aq. Br, neutralise with KOH soln. (20%) and add 1 ml of 0·1 or 0·25M-EDTA. If Cr is present, heat for 15 min. Add 1 ml of NH_4Cl - aq. NH_3 buffer (pH 11) and 1 ml of 0·3 or 0·75M-$CaCl_2$ and heat at 95° for 30 min. Centrifuge, decant the clear liquid and wash the pptd. group-3 hydroxides 3 times by centrifuging and decantation with slightly ammoniacal NH_4Cl soln. (2%). To the mixed decanted liquids add 0·5 ml of buffer soln. (pH 11) and 1 ml of thioacetamide soln. (2%), set aside for 30 min. and heat at 80° for 30 min. If Ni is present, carry out this pptn. in the presence of 0·5 ml of buffer soln., 1 ml of 4M-NH_4Cl and ⅓ twice the amount of thioacetamide required to precipitate the Zn. Centrifuge, wash the ppt. with slightly ammoniacal NH_4Cl soln. (2%) (3 × 1 ml), dissolve it in a few drops of 4N-HCl and boil to expel H_2S. If Cd is present, dilute to 0·3N in HCl, add 1 ml of thioacetamide soln. (2%), heat for 20 to 30 min. at 80° and remove the pptd. CdS. Heat the soln. of Zn^{2+} to 40° and neutralise to methyl red with 2N-NaOH. Add KCN soln. to mask Co and Ni and de-mask Zn by adding formaldehyde soln. To a 25-ml aliquot add 2 ml of NH_4Cl - aq. NH_3 buffer (pH 10) and 0·75 g of NH_4F and titrate with 0·001M-EDTA (disodium salt), with Eriochrome black T as indicator. H. N. S.

467. **Complexometric determination of zinc.** E. Hintzsche (VEB Chem. Werke Buna, Schkopau, Germany). *Chem. Tech., Berlin*, 1960, **12** (5), 272–280.—In the quick and accurate method described, the sample, in HCl soln., is added to Dowex 1-X10 resin and the Zn is separated from alkali and alkaline-earth metals, Ti, Al, Fe, Co, Mn, Sb, As, Cu and Pb (in the presence of Cu). The Zn is eluted from the resin with HNO_3 and titrated with 0·01N- or 0·1N-EDTA (disodium salt), with Eriochrome black T as indicator. The use of other indicators is discussed. (46 references.) E. M. MAYES

468. **Oxidations with potassium permanganate in presence of fluoride. II. Potentiometric titration of mercury(I) and the redox potential of the septavalent - tervalent manganese system.** I. M. Issa and M. Hamdy (Fac. of Sci., Cairo Univ.). *Anal. Chim. Acta*, 1960, **22** (6), 558–566.—The optimum conditions for the potentiometric titration of Hg^+ with $KMnO_4$ were found to be the use of N-H_2SO_4 and 0·4M-NaF and a temp. of 25° to 40°. Under these conditions up to 616 mg of Hg in 30 ml of soln. can be determined, which is an amount greater than can be determined by a visual method. Copper, as sulphate, is a convenient material for screening the colour of the manganic fluoride complex and in the titration of conc. soln., but a blank determination should be made. The error is < 0·7%. The reverse titration suffers from autodecomposition of the $KMnO_4$. At high acidities the titration is satisfactory with Cu^{II} present, the error being < 0·8%. The formal Mn^{7+}-Mn^{3+} redox potential (1·38N-H_2SO_4, 0·12N-NaF) is 1·4 V and increases with rise of acidity and decreases with increase in F^- concn. R. M. S. HALL

469. **Radiochemical analysis of aluminium of very high purity obtained by the zone-melting technique.** G. Chaudron. *Rec. Trav. Chim. Pays-Bas*, 1960, **79** (6), 502–509 (in French).—The application of the method to the determination of traces of impurities in aluminium of very high purity, with carriers for separating the various groups of elements, after irradiation of the sample with thermal neutrons, is outlined. Sulphides are pptd. from HCl soln. by H_2S, with Cu and As as collectors. The Al is separated by crystallisation of $AlCl_3.6H_2O$, which is obtained by saturating the soln. with HCl at 0°. Isotopes whose hydroxides are insol. are pptd. by aq. NH_3, after addition of La, Mn and Ga carriers. The rare-earth elements are separated from this group as oxalates, with La oxalate as carrier, and from this sub-group 10 rare-earth elements and Y and Sc are separated by ion exchange with Dowex-50 resin. From the original soln. the sulphides of Ni, Cd, Co and Zn are pptd. from ammoniacal soln. by saturation with H_2S; $CaCO_3$ and $SrCO_3$ are pptd., after addition of carriers of these elements, followed by separation of the perchlorates of K, Rb and Cs after addition of carriers. The residual soln. contains only Na. J. M. JACOBS

470. **Composition of aluminium nitrate - nitric acid mixtures by spectrophotometric measurements.** R. W. Henry and G. L. Booman (Philips Petroleum Co., Idaho Falls, U.S.A.). *Anal. Chem.*, 1960, **32** (7), 832–834.—Concn. of HNO_3 and Al in aq. soln. of HNO_3 and $Al(NO_3)_3$ can be determined from the extinctions measured at 295 mμ and 2·667 μ, respectively, in a 0·1-mm quartz cell at 25°. The procedure and precautions to be taken are described. The accuracy is within 0·03M for concn. of each in the molar range. The method is suitable for monitoring process-feed in nuclear-power plants, and its precision could be increased seven-fold by use of a single-beam, narrow band-width, filter instrument having an optimum damping circuit, because this would eliminate the unfavourable signal to noise ratio at 2·667 μ. W. J. BAKER

471. **Rapid method for the determination of gallium in nephelines.** V. K. Kuznetsov and N. A. Tananaev. *Izv. Vyssh. Uchebn. Zavedenii, Khim. i Khim. Tekhnol.*, 1959, **2** (6), 840–842; *Ref. Zhur., Khim.*, 1960, (14), Abstr. No. 56,694.—The sample is decomposed by heating with NH_4F [*Ref. Zhur., Khim.*, 1958, (7), Abstr. No. 21,201] with subsequent photometry of Ga as the complex with rhodamine B (C. I. Basic Violet 10) in benzene [*Ref. Zhur., Khim.*, 1956, (6), Abstr. No. 16,371]; acetone is added to the HCl soln. before the extraction to increase the degree of extraction of the complex into the benzene. *Procedure*—Mix 0·1 to 0·2 g of finely ground sample in a platinum crucible with five times the amount of powdered NH_4F and heat for 5 min. at 300° to 400°; extract the melt by heating with 6N-HCl and make up to 25 ml with 6N-HCl. Add a 10 or 20% $TiCl_3$ soln. to 1 or 2 ml of the test soln. till the interfering elements Fe^{III}, Sb^{V}, Tl^{III} and Au^{III} are completely reduced, then add the same amount of HCl (sp. gr. 1·19), dilute to 3 ml with 6N-HCl, and set aside for 5 min. Add 0·4 ml of a 0·5% rhodamine B soln. in 6N-HCl and 1 ml of acetone, shake while cooling, then add 5 ml of benzene, shake for 1 to 2 min., and set aside for 10 min. Measure the extinction with a green filter (540 to 570 mμ). Use standard soln. containing 0·001 to 0·01 mg of Ga per ml to construct a calibration curve. Even considerable amounts of F do not interfere. The method can be used to determine Ga in many silicates that are decomposed by NH_4F. C. D. KOPKIN

472. **Determination of gallium and indium in glycerol plating baths.** E. P. Cocozza (Lansdale Tube Co., Lansdale, Pa., U.S.A.). *Chemist Analyst*, 1960, **49** (2), 46.—The alloy plating soln., which contains gallium and indium chloride in a molar ratio of about 1:25, is diluted and made 6N in HCl. The Ga is extracted with ether saturated with HCl. The two metals are then determined separately by titration with EDTA, with a Cu - PAN indicator. G. BURGER

473. **Oxidation with manganate solutions. IV. Determination of monovalent thallium.** I. M. Issa and M. G. E. Allam (Fac. Sci., Cairo and Assiut Univ., Egypt). *Z. anal. Chem.*, 1960, **175** (6), 421–428 (in English).—In the titration of Tl^+ with alkaline K_2MnO_4 soln. the end-points (detected electrometrically) occurred too early, and errors of 1·38 to 8·1% were observed. Better results were obtained in the presence of telluric acid, the errors then amounting to ≃ 1·5 % at 20°. The errors were reduced still further by accelerating the rather sluggish reaction by adding NaCl and heating to 50°. In the titration of MnO_4^{2-} with Tl^+ the presence of telluric acid was again necessary to obtain accurate results. It was found that Tl^+ could be determined by adding an excess of alkaline manganate soln., and back-titrating the excess with sodium arsenite soln. R. M. ROWLEY

474. **Micro-determination of thallium.** I. P. Alimarin and I. Krausz (Inst. Inorg. and Anal. Chem., L. Eötvös Sci. Univ., Budapest). *Magyar Kém. Foly.*, 1960, **66** (7), 262–263.—Two methods are described, the determination range in each being 0·3 to 2·0 mg of Tl^I. In the first method (gravimetric) the Tl is pptd. with Na tetraphenylborate (**I**) from neutral soln. in the presence of Na acetate. After drying (120°), the ppt. has the composition $TlB(C_6H_5)_4$. Zinc and Cd do not interfere. In the second (volumetric) method a known amount of standard **I** soln. is added to the thallium soln. and the excess of **I** is titrated with standard $AgNO_3$ soln., with eosin as indicator. Both analytical procedures are given in detail and results are tabulated. B. VASZKO

475. **Chromatographic separation of the rare-earth metals with tributyl phosphate.** L. I. Martynenko, G. K. Eremin and A. I. Kamenev. *Zhur. Neorg. Khim.*, 1959, **4** (11), 2639; *Ref. Zhur., Khim.*, 1960, (8), Abstr. No. 30,416.—Dispersion chromatography is used, with silica gel (**I**) as adsorbent and tributyl phosphate satd. with 12N-HNO_3 (**II**) as eluent. A satd. soln. of the mixed nitrates of the cerium sub-group in **II**, containing about 8 g of M_2O_3 in 100 ml, is introduced into the upper part of a column (diam. 33 mm) filled to a height of 85 cm with pure **I** (particle size 0·25 to 1·0 mm) and the column is eluted with **II** at a rate of flow of 2 cm per min. The mixture is separated fairly cleanly into its components. The eluate contains up to 20 g of M_2O_3 per litre. C. D. KOPKIN

476. **Reducing properties of cerous ion in alkaline media.** N. H. Furman and A. J. Fenton, jun. (Univ., Princeton, N.J., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 745–747.—Quantities of $Fe(CN)_6^{4-}$ as small as 0·6 mg can be determined accurately by titration with Ce^{3+} in 25 to 60% aq. K_2CO_3 soln. in a stream of CO_2 at ≃ 25°. The end-point can be obtained potentiometrically or amperometrically, but titration to a pre-set potential (+80 mV *vs.* the S.C.E.) is preferred. The titration of MnO_4^- can also be made by this procedure but, because of pptn. of gelatinous MnO_2 on the electrodes, 10 to 15 min. is required per titration. Glucose (< 3 mg per 5 ml) can be determined indirectly by the addition of 0·025N-$K_4Fe(CN)_6$ in excess and ≃ 4M-aq. K_2CO_3, followed, after heating the mixture to 100° for 15 min., by back-titration of the excess of $K_4Fe(CN)_6$ with 0·01N-$Ce_2(SO_4)_3$. W. J. BAKER

477. **Spectrophotometric determination of yttrium with catechol violet.** J. P. Young, J. C. White and R. G. Ball (Anal. Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1960, **32** (8), 928–930.—Yttrium reacts with catechol violet in the pH range 8·4 to 9·0 giving an intense colour (absorption max. at 665 mμ, molar absorptivity 25,900), which is stable for at least 8 hr. A preliminary extraction with tri-n-octylphosphine oxide enables Y to be determined in the presence of Fe, Mo, U, Zr and Th. Neodymium and Sm react similarly to Y and it is suggested that other rare-earth elements would behave in the same manner. T. R. ANDREW

478. **Determination of oxygen in yttrium fluoride by a vacuum distillation technique.** V. M. Horrigan, V. A. Fassel and J. W. Goetzinger (Inst. Atomic Res., Iowa State Univ., Ames, U.S.A.). *Anal. Chem.*, 1960, **32** (7), 787–789.—The sample (100 to 200 mg as pellets wrapped in 300 mg of platinum foil) is inserted into a vacuum-fusion furnace at ≃ 600°, the temp. is raised slowly to 1850° and held there for 45 to 60 min. to permit complete distillation of YF_3, leaving the less volatile Y_2O_3 and YOF to be reduced by the graphite crucible. The evolved CO is measured manometrically. The recovery of total O is quant. if the reduction takes place in a liquid, *viz*, molten platinum; the coeff. of variation is about 8% (five analyses of mixtures of YF_3 - Y_2O_3 and YF_3 - YOF). The effect of platinum on the rate of evolution of CO is discussed.
W. J. BAKER

479. **Polarographic determination of traces of europium in minerals and ores.** V. T. Athavale, R. G. Dhaneswar and M. M. Mehta (Atomic Energy Est. Trombay, Bombay, India). *Anal. Chim. Acta*, 1960, **23** (1), 71–73.—Total rare-earth metals are recovered as chlorides from the mineral sample (0·5 to 2 g) by conventional methods, Pb being removed as $PbSO_4$. The mixture is dissolved in water, 2·5 ml of M-NH_4Cl is added, the soln. is diluted to 25 ml and a polarogram is recorded. Reduction of Eu^{3+} to Eu^{2+} takes place at $E_{\frac{1}{2}} = -0{\cdot}67$ V *vs.* the S.C.E., and other rare-earth metals do not interfere. The method is suitable for the determination of Eu contents down to 10 p.p.m. H. N. S.

480. **Determination of bound and free carbonic acid. I. Micro-determination of alkali carbonate and hydroxide in the presence of each other.** E. Schulek and A. Endröi-Havas (Inst. Inorg. and Anal. Chem., L. Eötvös Univ., Budapest, Hungary). *Z. anal. Chem.*, 1960, **175** (4), 241–244 (in German).—In the titration of dil. acids or bases with phenolphthalein (**I**) as indicator, interference by aerial CO_2 may be excluded by covering the mixture with a layer of pentane containing propane and butane, the high vapour pressure of which provides an inert atmosphere. Addition of more **I** near the end-point is advisable as fission in alkaline media of the lactone ring in **I** may induce decolorisation. Thus 0·01N-HCl or NaOH may be titrated with increased accuracy. In the determination of carbonates by pptn. with $Ba(OH)_2$, hydrolysis of $BaCO_3$ is prevented by addition of $BaCl_2$ and ethanol. (*Cf. Anal. Abstr.*, 1961, **8**, 66.) J. P. STERN

481. **Determination of metal cyanide and thiocyanate complexes by Kjeldahl - Gunning and Carius sealed-tube digestion methods.** B. Jaselskis and J. G. Lanese (Univ. of Michigan, Ann Arbor, U.S.A.). *Anal. Chim. Acta*, 1960, **23** (1), 6–10.—Results from the Kjeldahl method are of poor reproducibility, and the Carius method is preferred. The sample (10 to 25 mg), mixed with 50 mg of a mixture of HgO and $HgSO_4$ and 2 ml of conc. H_2SO_4 satd. with $HgSO_4$, is heated in a sealed tube for 2 hr. at 315°. After opening the tube, SO_2 is removed by boiling. The cooled liquid is diluted with water, 150 mg of EDTA (disodium salt) is added to sequester metals that form complexes with NH_3, the soln. is made alkaline with NaOH soln. containing $Na_2S_2O_3$, and the NH_3 is recovered by distillation and titrated with standard HCl.
H. N. S.

482. **Extraction procedure for the colorimetric determination of silica.** H. N. Wilson and J. M. Skinner. *Rec. Trav. Chim. Pays-Bas*, 1960, **79** (6), 574–581 (in English).—The silica is converted into 12-molybdosilicic acid with sodium molybdate and then extracted with a 1% solution of tri-isodecylamine in toluene. The extinction at 400 mμ is then measured in a 1-cm cell. The results of determinations of silica in samples of anhydrite, firebrick, etc., by this method and gravimetrically, are compared. The method is not of the highest accuracy, but has been successfully applied to larger amounts of silica than have previous colorimetric methods. J. M. JACOBS

483. **Combined gravimetric and photometric procedure for determining silica in silicate rocks and minerals.** P. G. Jeffery and A. D. Wilson (D.S.I.R., Lab. of the Gov. Chemist, Geological Survey and Museum, London). *Analyst*, 1960, **85**, 478–485.—The greater part of the silica is determined by the usual method, *i.e.*, fusion with Na_2CO_3, digestion of the melt with water, evaporation of the liquid with conc. HCl and collection of the SiO_2 by filtration. The combined filtrate and washings are adjusted to 200 ml, a 5-ml aliquot is diluted to ≃ 15 ml, 1 ml of a 10% (w/v) soln. of ammonium molybdate in N-aq. NH_3 is added and, after 10 min., 5 ml of 10% aq. oxalic acid soln. and 2 ml of a reducing soln. (0·05 g of 1-amino-2-naphthol-4-sulphonic acid, 0·7 g of Na_2SO_3 and 9 g of $Na_2S_2O_5$ per 100 ml of water). The liquid is diluted to 100 ml and, after ≮ 30 min. (preferably 1 hr.), the extinction of the blue liquid is measured at 650 mμ and referred to a calibration graph constructed with a standard soln. of SiO_2 (prep. described). Beer's law is obeyed and there is no interference from Fe (≯ 20% of Fe_2O_3), TiO_2 (≯ 8%) or P_2O_5 (≯ 10%). Methods for removal of larger amounts of Fe and Ti are described. A. O. JONES

484. **Spectrographic analysis of high-purity silicon carbide.** G. H. Morrison, R. L. Rupp and G. L. Klecak (General Telephone and Electronics Laboratories Inc., Bayside, N.Y.). *Anal Chem.*, 1960, **32** (8), 933–935.—By using a selective volatilisation technique and controlled exposure times dependent on the elements sought, the background due to SiC is greatly reduced and enables small concentrations of impurities in SiC to be determined. The apparatus is the same as reported previously (Rupp *et al.*, *Anal. Abstr.*, 1961, **8**, 595) and an atmosphere of Ar is used. Impurity elements are determined in the range 0·01 to 10 p.p.m. Distillation times, with a 20-amp. d.c. arc are—for As, Bi, Cd, Ga, Hg, In, Na, P, Pb, Sb, Sn, Tl and Zn, 6 sec.; for Ag, Al, Be, Ca, Cr, Cu, Ge and Mn, 25 sec.; for Co, Fe, Mg, Ni, Ti and V, 60 sec.; for Mo, 15 to 35 sec.; and for Zr, 35 to 50 sec. Germanium dioxide (10 p.p.m.) is added as an internal standard for the first two groups, and silicon serves as internal standard for the other groups. T. R. ANDREW

485. **Determination of germanium in molybdenites and other sulphides.** S. A. Dekhtrikyan. *Dokl. Akad. Nauk ArmSSR*, 1959, **28** (5), 213–216; *Ref. Zhur., Khim.*, 1960, (8), Abstr. No. 30,469.—Mix 0·5 to 1 g of sulphide mineral in a porcelain dish with 0·5 g of CaO, add 6 to 8 ml of satd. KNO_3 soln., evaporate to dryness on a water bath, carefully heat to 550° to 600° with occasional stirring, and ignite to a white powder. Cool, add 5 to 6 ml of H_3PO_4 and 5 ml of water, heat first on a water bath and

then on a sand bath to a syrupy consistency, cool, add 25 ml of water and 75 ml of 12N-HCl and extract Ge with CCl_4. Determine Ge by the phenylfluorone method. The method is almost twice as rapid as the usual fusion method and platinum vessels are not necessary. The method can be used to determine Ge in molybdenite, molybdenum concentrates, enargite, sphalerite, chalcopyrite, pyrite and bornite. C. D. KOPKIN

486. **Controlled-potential coulometric determination of tin.** A. J. Bard (Dept. of Chem., Harvard Univ., Cambridge, Mass., U.S.A.). *Anal. Chim. Acta*, 1960, **22** (6), 577–582 (in English).—The reduction of Sn^{IV} to Sn^{II} is unsatisfactory, but the reduction of Sn^{II} to the metal at a mercury or tin amalgam electrode is quantitative. If a stannic soln. is stirred with a tin amalgam electrode reduction to Sn^{II} occurs, thus obviating the first reduction stage by electrolysis. The supporting electrolyte is 3·3M in NaBr and 0·2N in HCl, and the reduction is carried out at −0·5 to −0·7 V *vs.* the S.C.E. Lead interferes, but pre-reduction at −0·4 V eliminates interference due to Cu, Sb and Bi. The error is < 0·25%. R. M. S. HALL

487. **Separation of tin, antimony and tellurium on anionites.** V. N. Rŷbakov and I. I. Stronskiĭ. *Zhur. Neorg. Khim.*, 1959, **4** (11), 2449–2451; *Ref. Zhur., Khim.*, 1960, (8), Abstr. No. 30,419.—An earlier method is used [*Ref. Zhur., Khim.*, 1956, (14), 43,496], based on the sorption of $SnCl_6^{2-}$, $SbCl_6^-$ and $TeCl_6^{2-}$ on a strongly basic anionite with subsequent elution of Sb^V with 3N-HCl, Te^{IV} with N-HCl, and Sn^{IV} with 1·8N-$HClO_4$. The column (height 100 mm × diam. 2 mm) is filled with 100 to 150 mg of the anionite (Cl^- form) (grain size 30 μ). Mixtures of Te and Sb can be separated on EDE-10P or ASD-2 (a new strongly basic anion exchanger prepared from trimethylhydrazine and polystyrene). All three elements cannot be separated on EDE-10P, since Sn and Sb are eluted together, but three-component mixtures can be separated on ASD-2; Sb is completely eluted with 2 ml of 3N-HCl, Te with 2·2 ml of N-HCl, and Sn with 1 ml of 2N-$HClO_4$. The separation takes about 3 hr. Similar results are obtained with Dowex 1-X8. Contamination of each fraction by the other elements does not exceed 0·03% of its initial quantity. C. D. KOPKIN

488. **Determination of very small quantities of lead.** R. R. Marshall and D. C. Hess (Enrico Fermi Inst. for Nuclear Studies, Univ. of Chicago, Ill., U.S.A.). *Anal. Chem.*, 1960, **32** (8), 960–966.—A procedure is described for the determination of as little as 0·01 p.p.m. of Pb in 20 to 25 g of crushed rock or meteorite. The sample is loaded into a graphite crucible containing 5·5 or 11 μg of ^{206}Pb-rich lead, and heated to 1400° in a stream of N, the volatilised Pb being collected on a water-cooled quartz tube. The deposit is dissolved in HNO_3 and the total Pb is determined photometrically with dithizone. Organic matter is then destroyed and the residue is transferred to a tantalum filament with a few drops of boric acid soln. A lead - boric acid glass is formed by heating, and the ratios of ^{206}Pb:^{204}Pb:^{207}Pb:^{208}Pb are determined in a solid-sample mass spectrometer. A survey has been made of the degree of Pb contamination from a number of sources (*e.g.*, distilled water and reagents). T. R. ANDREW

489. **Enhancement of sensitivity in the spectral isotopic analysis of lead.** M. S. Kashtan, E. V. Sobotovich and T. N. Khlopina. *Optics and Spectroscopy*, 1960, **8** (1), 11–13; English translation from *Optika i Spektroskopiya*, 1960, **8** (1).—The investigation described is concerned with the isotopic analysis of Pb from studies of the hyperfine structure of the spectral line Pb I 4057·8 A. The spectrum is excited in a hollow-cathode discharge and investigated with a photo-electric recording spectrometer in conjunction with a Fabry-Perot etalon. The preferred form of the sample and the most effective way in which it is introduced into the hollow-cathode discharge are the main topics discussed. B. S. COOPER

490. **Determination of lead in industrial alloys. Precipitation as lead sulphate in homogeneous solutions.** F. Burriel-Martí and M. J. Gárate. *Rec. Trav. Chim. Pays-Bas*, 1960, **79** (6), 495–501 (in French).—Lead is pptd. quant. from soln. of its alloys (containing Sn and Pb) in a mixture of dil. aq. HNO_3 and HF by digesting the soln. on a water bath with sulphamic acid in the presence of ethanol. The crystals are larger and more perfectly formed the greater the amount of dil. HNO_3 present. J. M. JACOBS

491. **Simultaneous polarographic determination of lead and azide ions of lead azides in aqueous media.** J. I. Bryant and M. D. Kemp (Army Engineer Res. and Devel. Lab., Fort Belvoir, Va., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 758–760.—Concn. of Pb^{2+} and N_3^- in aq. $Pb(N_3)_2$ (10^{-3} to 2×10^{-4}N) can be determined simultaneously in ≃ 10 min. by polarographing the de-aerated sample soln., in 0·1N-KNO_3 as supporting electrolyte, at the dropping-mercury electrode at 25°. A mercury - mercurous sulphate reference electrode acidified with H_2SO_4 is used, and 0·002% of Triton X-100 is added to the soln. to ensure sharp separation of waves. The $E_{\frac{1}{2}}$ *vs.* the S.C.E. are +276 and −381 mV for N_3^- and Pb^{2+}, respectively. The method must be standardised against gravimetric determinations as AgN_3. The error is within ±1%. W. J. BAKER

492. **Determination of titanium according to the Dutch tentative standard V 3104.** M. Oosting [Ferro Enamels (Holland) N.V., Rotterdam, Netherlands]. *Chem. Weekbl.*, 1960, **56** (28), 423–424.—In the indirect determination of Ti^{IV}, which is based on the reduction of Ti^{IV} to Ti^{III} with a cadmium reductor, followed by oxidation of Ti^{III} with $Fe_2(SO_4)_3$ and titration of the Fe^{III} formed with $Ce(SO_4)_2$ or $KMnO_4$, two errors occur, which compensate each other, *viz.* Ti^{IV} is reduced too far, and part of the Fe^{II} formed is oxidised by air. These errors can be overcome by carrying out a direct determination with exclusion of air. M. J. MAURICE

493. **Potentiometric determination of titanium in presence of aluminium.** L. Giuffrè and F. M. Capizzi (Polytech., Milan, Italy). *Ann. Chim., Roma*, 1960, **50** (3–4), 405–412.—A rapid method for the determination of Ti in complex aluminium - titanium polymerisation catalysts is proposed. The materials are treated with H_2SO_4 - HNO_3 and the metal sulphates thus produced are dissolved in 3% aq. H_2O_2 soln. The pH is adjusted to 1·8 to 1·9, and an excess of 0·1M-EDTA (disodium salt) over that required to form the Ti - H_2O_2 - EDTA complex is added. The excess of EDTA is then determined by potentiometric titration at 0° with 0·01N-$(NH_4)_2SO_4.Fe_2(SO_4)_3$, continuously

adjusting the pH with aq. Na acetate soln. Alternatively, the titration may be carried out with salicylic acid as indicator. L. A. O'NEILL

494. **Extraction and separation of zirconium and hafnium by means of liquid anionic exchangers in a hydrochloric acid medium. I. Behaviour of some primary, secondary and tertiary amines.** E. Cerrai and C. Testa (CISE, Milan, Italy). *Energia Nucleare*, 1959, **6** (11), 707–716 (in English).—A group of long-chain amines, including primary, secondary and tertiary, were tested for their ability to extract Zr and Hf from HCl soln. The distribution coeff. between the organic and aq. phase were determined and the separation factor (S.F.) was calculated.

II. Extraction with tri-n-octylamine. E. Cerrai and C. Testa. *Ibid.*, 1959, **6** (12), 768–780.—A detailed study of the following factors has been made—(*i*) concn. of HCl in the aq. phase; (*ii*) nature of the diluent (kerosine, cyclohexane, benzene or trichloroethylene); (*iii*) concn. of Zr and Hf in the initial soln.; (*iv*) concn. of the amine in the diluent; (*v*) total amount of amine; (*vi*) contact time; (*vii*) extraction isotherm; (*viii*) temp.; (*ix*) Cl^- and H^+ concn.; and (*x*) presence of other acids. N. E.

495. **Polarographic determination of nickel, chromium and tin in Zircaloy and zirconium metal.** V. T. Athavale, R. G. Dhaneswar and M. M. Mehta (Atomic Energy Est. Trombay, Bombay, India). *Anal. Chim. Acta*, 1960, **23** (1), 74–77.—The sample (5 g) is dissolved in 40% HF, the soln. is heated to fuming with conc. H_2SO_4, and 10 ml of conc. H_2SO_4 and sufficient water to produce 100 ml are added. Soln. for polarography of the metals are prepared as follows. *Nickel*—To 5 ml of the sample soln. add 15 ml of water and 2 to 3 ml of conc. H_2SO_4 and precipitate the Zr with 14 ml of 13M-pyridine. Filter, wash the ppt. with dil. pyridine (5% v/v), dilute the filtrate to 50 ml and record a polarogram for $E_{\frac{1}{2}} = -0{\cdot}925$ V *vs.* the S.C.E. *Chromium*—To 20 ml of soln., containing 0·25 to 1 g of alloy, add 4 g of Na_2O_2 slowly, then add 10 to 20 ml of water, boil, cool and filter. Wash the ppt. with dil. NaOH soln., concentrate the filtrate and adjust to 25 ml. *Tin*—Precipitate the Sn as SnS_2, fuse the ppt. with bisulphate, leach with 2N-HCl, add 21 g of NH_4Cl and 2 ml of 0·5% gelatin soln., dilute to 100 ml and record the polarogram (*cf.* Allsop and Damerell, *Brit. Abstr. C*, 1949, 376). H. N. S.

496. **Complexometric titration of thorium using some azo-dyes from chromotropic acid.** S. K. Datta (Victoria Government Coll., Coochbehar). *J. Sci. Ind. Res., B, India*, 1960, **19** (5), 168–170.—2-(5-Sulphonaphthylazo)- (**I**), 2-(6-sulphonaphthylazo)- (**II**) and 2-(4-carboxy-3-hydroxyphenylazo)-1,8-dihydroxynaphthalene-3,6-disulphonic acid (**III**) are used as indicators (1·5 ml of 0·05% soln. for 30 ml of titrant) in the titration or back-titration of thorium soln. with EDTA (disodium salt) up to 40°. Optimum pH values (acetate buffer) are, for **I**, pH 3; for **II**, pH 2·5 to 2·8; and for **III**, 2·4 to 3·0. The colour changes in the direct titration are, for **I**, blue - violet to pinkish red; for **II**, pinkish blue to reddish pink; and for **III**, pinkish violet to deep red. Tervalent Fe, Zr^{4+}, Ce^{4+}, Sn^{2+}, Ag^+, Cu^{2+}, Al^{3+}, PO_4^{3-}, F^- and oxalate interfere; Fe^{2+} interfere when **I** and **II** are used as indicators, but the titration can be carried out with **III** as indicator. Tervalent Fe can be reduced to Fe^{2+} with ascorbic acid. E. J. H. BIRCH

497. **Rapid photometric determination of thorium with Thoron II.** V. I. Kuznetsov and S. B. Savvin. *Radiokhimiya*, 1959, **1** (5), 583–588; *Ref. Zhur., Khim.*, 1960, (8), Abstr. No. 30,474.—Thoron II [3,3′-di-(2-hydroxy-3,6-disulpho-1-naphthylazo)biphenyl-4,4′-diarsonic acid] (**I**) forms more stable complexes than Thoron I, and can be used for the determination of Th in the presence of sulphates and phosphates. **I** gives colour reactions with Th, U^{VI}, Zr, Hf, Ti, Bi, Pb, Ca and the rare-earth elements; the colours are similar to those produced with Thoron I. With **I**, 0·1 to 0·2 μg of Th per ml can be determined, and 5 μg of Th in 25 ml is determined with an error ≯ 5%. Fuse the sample, containing 5 to 200 μg of ThO_2, with 0·50 ± 0·05 g of $K_2S_2O_7$, dissolve the melt in 10 to 15 ml of HCl (1:4), filter, add 5·5 ml of conc. HCl, 1 ml of 3% oxalic acid soln. and 1 ml of 0·25% aq. **I** soln., make up to 25 ml with HCl (1:4), and measure the extinction in 10-mm cells at 554 mμ or in 50-mm cells in a photometer with a green filter. (44 references.) C. D. KOPKIN

498. **Determination of thorium in fluoride salt mixtures.** R. F. Apple and J. C. White (Anal. Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Chemist Analyst*, 1960, **49** (2), 42–43.—In mixtures containing the fluorides of Li, Be, U and Th, Th can be determined by the back-titration of an excess of EDTA at pH 4 with 0·01M-Cu^{II}, with xylenol orange as indicator. Fluoride is first removed as boron trifluoride by heating a soln. of the sample in $HClO_4$ - H_2BO_3. If Ce is present, the F^- are removed and the Th is extracted from a soln. in 6M-HCl by means of tri-n-octylphosphine oxide in cyclohexane. A modification of the procedure permits the determination of Th in amounts between 200 and 1000 μg. G. BURGER

499. **Gravimetric determination of ammonium as ammonium tetraphenylborate: a critical study.** F. E. Crane, jun., and E. A. Smith (Douglass College and Rutgers Graduate School, State Univ., New Brunswick, N.J., U.S.A.). *Chemist Analyst*, 1960, **49** (2), 38–40.—The optimum conditions for the semi-micro pptn. of NH_4^+ have been established, namely, a pH of 1 to 3 before the addition of tetraphenylborate ion; the use of a 25 to 50% excess of tetraphenylborate ion; the presence of an inert salt; a temp. of 20° to 25°; time of digestion ≯ 1 hr.; the use of 1% aq. formic acid followed by water or water satd. with ammonium tetraphenylborate for washing; and careful drying of the ppt. at 100°.
G. BURGER

500. **Quantitative bromatometric oxidation of ammonium compounds and formaldehyde in acid medium with decinormal potassium bromate.** D. Kőszegi and E. Salgó. *Magyar Kém. Foly.*, 1960, **66** (4), 142–147.—*Cf. Anal. Abstr.*, 1959, **6**, 3025.

501. **Detection and spectrophotometric determination of hydrazine and its derivatives with vanillin.** J. Práchenská and J. Zýka (Dept. Anal. Chem., Charles' Univ., Prague). *Chem. Průmysl*, 1960, **10** (7), 343–346.—Hydrazine and its derivatives (semicarbazide, phenylhydrazine) react with vanillin to give a yellow coloration, which is particularly intense in u.v. light. *Detection*—Apply a soln. of the sample to filter-paper, dry under an i.r. lamp, then add vanillin soln. (1% in 96% ethanol) (1 drop), dry, and add HCl soln. (10% in ethanol) and observe the yellow colour in u.v. light. The sensitivities were—pD = 6·68 (for hydrazine), pD 5·0

(semicarbazide) and pD 4·77 (phenylhydrazine); large amounts of urea, NH_4^+, NO_3^- or hydroxylamine do not interfere. *Spectrophotometric determination*—To a 25-ml flask add 0·5 to 10 ml of the sample containing 1 to 10 μg of hydrazine or 0·1 to 1 mg of semicarbazide, and then acid till the soln. contains 3% of H_2SO_4, 1·5% of HCl, 2·5% of $HClO_4$, 5% of H_3PO_4 or 20% of acetic acid. Add vanillin soln. (2% in methanol) (5 ml), mix, dilute with H_2O to vol. and after 10 min. measure the extinction at 420 mμ. Carry out a blank. J. ZÝKA

502. **Permanganometric determination of hydroxylamine via copper(II) catalysis.** K. Bhaskara Rao (Central Lab., Hindustan Aircraft Ltd., Bangalore, India). *Chemist Analyst*, 1960, **49** (2), 40.—In the presence of sufficient Cu^{2+}, hydroxylamine (**I**) can be titrated in 0·2 to 0·4M-HCl at 70° to 75° with 0·1N-$KMnO_4$. The soln. should contain $\gtrsim$ 0·15 millimole of **I** and the mol. ratio of **I** to Cu should be 1:15. The recovery of **I** is 99·7%.
G. BURGER

503. **New reagents for the colorimetric determination of microgram quantities of nitrite.** L. S. Bark and R. Catterall (Roy. Tech. Coll., Salford, England). *Mikrochim. Acta*, 1960, (4), 553–558 (in English).—In the presence of HNO_2, the hydrochlorides of *N*-(2-aminophenyl)-morpholine (**I**) and -piperidine (**II**) give intensely orange diazonium compounds. At 18° the compound derived from **I** (absorption max. at 435 mμ) forms immediately and that from **II** (max. at 445 mμ) within 40 min. Loss of extinction at room temp. in the dark is $< 1\%$ in 24 hr. The reaction is sensitive to 0·05 μg per ml with the use of a 1-cm cell and reproducible to within $\pm$ 0·05 μg per ml; soln. containing $\gtrsim$ 20 μg of NO_2^- per ml can be analysed. Oxidising agents cause a red coloration (max. at 510 mμ) and interfere. J. P. STERN

504. **Impregnation test for detecting trace amounts of orthophosphate.** R. Antoszewski and J. S. Knypl (Dept. of Plant Physiol., Univ. of Łódź, Poland). *Analyst*, 1960, **85**, 527–528.—A strip of Whatman No. 1 or 4 chromatography paper is dipped into an aq. 15% soln. of ammonium molybdate, allowed to dry and then dipped into a 4% soln. of quinoline in 0·6N-HCl. The strip is washed three times with water and allowed to dry. The sample soln., if alkaline, is acidified with H_2SO_4, HCl, HNO_3 or $HClO_4$; if it is strongly acid it is diluted, and if it is neutral the paper is sprayed with a 1·25% soln. of H_2SO_4 and allowed to dry. The sample soln. (1 drop) is placed on the paper which is heated at 98° to 100° for $\simeq$ 1 min. and allowed to dry. If PO_4^{3-} are present a yellow spot appears, faintly perceptible in daylight, but more so in u.v. light. It can be made visible in daylight by spraying the paper with or immersing it in Ilford ID2 developer. The benzidine test of Feigl can also be applied. The procedure permits the detection of $1{\cdot}5 \times 10^{-9}$ g of P. Salts and organic compounds in concn. > 100 times that of PO_4^{3-} do not interfere, but the spots are obscured by silicate and arsenate in amounts respectively 20 and 100 times that of PO_4^{3-}.
A. O. JONES

505. **Gravimetric determination of phosphates.** E. Schulek and Á. Éndrői (Inst. for Inorg. and Anal. Chem., L. Eötvös Sci. Univ., Budapest). *Magyar Kém. Foly.*, 1960, **66** (4), 139–142.—An investigation was made of the pptn. of phosphate as $MgNH_4PO_4.6H_2O$ and $(NH_4)_3P(Mo_3O_{10})_4$, in the presence of various elements. Contamination of the ppt. was checked and Mg, NH_4^+, Ca, K, Na, Fe and Al were determined quant. by means of flame-spectrophotometric, spectrographic and chemical methods. It was shown that the separation of phosphate with magnesia mixture by the Winkler procedure is not affected by relatively large amounts of K^+ and Na^+. The disturbing action of Fe and Al in amounts not exceeding 1% can be eliminated by the addition of EDTA. An accurate procedure is described for the determination of phosphate in the presence of Ca, in which the Ca is masked with EDTA, so that the troublesome separation as $(NH_4)_3P(Mo_3O_{10})_4$ is avoided; the Ca can be previously determined by direct complexometric titration. B. VASZKO

506. **Phosphate analysis with the Technicon AutoAnalyser. Selective orthophosphate and total inorganic phosphate determinations.** D. P. Lundgren (Res. and Devel. Div., Lever Bros. Co., Edgewater, N.J., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 824–828.—Orthophosphate and total inorganic phosphate in soln. containing condensed phosphates can be determined colorimetrically at the rate of 20 samples per hr., the standard deviation of a single measurement being $\simeq \pm 1\%$. The method is comparatively free from interference and should be applicable to other problems in phosphate analysis.
K. A. PROCTOR

507. **Iodimetric determination of arsenic in technical calcium arsenate.** S. A. Kiss (Borsodi Vegyi Kombinát, Kazincbarcika, Hungary). *Z. anal. Chem.*, 1960, **175** (2), 81–84 (in German).—The method is based on the pptn. of As^V as $MgNH_4AsO_4$, which is filtered off, dissolved in H_2SO_4 and treated with KI; the liberated iodine is titrated with $Na_2S_2O_3$. The interference by Fe^{3+} is masked by the addition of K Na tartrate. *Determination of total As*—To the acid or neutral soln. (10 to 20 ml) containing 0·03 to 0·1 g of As are added 1 g of $KClO_4$ and 5 ml of conc. HCl and the mixture is boiled for a few minutes. At room temp. are added 10 ml of K Na tartrate soln. (M), 10 ml of $MgCl_2$ soln. (55 g of $MgCl_2.6H_2O$ and 105 g of NH_4Cl per litre, slightly acidified with HCl), and the mixture is treated dropwise with 10% aq. NH_3 from a burette until the first crystals of the arsenate ppt. appear. The mixture is swirled and, after 5 min., 10 ml of conc. aq. NH_3 is added. After 30 min., the ppt. is filtered off and washed with wash liquid (3% of NH_4NO_3 in 10% aq. NH_3) (5 × 5 ml). The ppt. and filter-paper are transferred to a flask containing 25 ml of H_2SO_4 (10%) and 0·1 g of $KHCO_3$, and stirred, then 5 g of KI is added, and after 2 min. the mixture is titrated with 0·1N-$Na_2S_2O_3$, with starch soln. (0·5%) as indicator. In the determination of As^V the addition of $KClO_4$ is omitted and the difference of the two titrations gives As^{III}. The method described can also be used to determine 0·005 to 0·03 g of As; 10 ml of 0·1N-K_2HPO_4 must then be added before the soln. is made alkaline with aq. NH_3. B. B. BAUMINGER

508. **Titrimetric determination of antimony.** M. R. Thompson. *Metallurgia, Manchr*, 1960, **61**, 283–285.—The literature published since 1953 is reviewed. (35 references.) S.C.I. ABSTR.

509. **Rapid determination of free sulphur and sulphides in technical antimony sulphide.** D. Prístavka (Dept. Anal. Chem., Inst. Chem. Technol.,

Bratislava, Czechoslovakia). *Chem. Zvesti*, 1960, **14** (6), 422–424.—Elementary sulphur is determined by a rapid cold extraction with freshly distilled CS_2, and Sb_2S_5 is determined indirectly by decomposing it at 290° to 300° into Sb_2S_3 and elementary sulphur, which is vaporised. J. ZÝKA

510. **Micro-analysis of vanadium. I. Detection of vanadium(V) by column chromatography.** I. Krausz (Inst. for Inorg. and Anal. Chem., L. Eötvös Sci. Univ., Budapest). *Magyar Kém. Foly.*, 1960, **66** (6), 218–219.—The presence of traces of V^V in soln. is detected by passage through a glass chromatographic column packed with silica gel - 8-hydroxyquinoline (3:1). The sensitivity of the method was assessed in the presence of Cr^{VI}, Mo^{VI}, W^{VI}, Cu^{II}, Pb, Bi, Cd, Sr, Ba, K, Na, Mg, Zn, Mn^{II}, Cr^{III}, Al, NH_4^+, SO_4^{2-}, Cl^-, NO_2^-, PO_4^{3-} and borate. In most cases the limit of detection is 1 to 2 μg. The effect of pH was investigated, the most favourable range being 1·4 to 6·7.

II. Detection of vanadium(V) by paper chromatography. I. Krausz. *Ibid.*, 1960, **66** (8), 296–297.—The solution containing V^V is treated with 8-hydroxyquinoline and the resulting ppt. is extracted with $CHCl_3$, the extract is concentrated, and applied to a chromatographic column packed with paper. After drying the column, it is eluted with a mixture of isoamyl alcohol and 2N-acetic acid (1:1) at a speed of 30 to 40 mm per hr. The R_F value for the V 8-hydroxyquinolinate is 0·88. In the presence of Pb, Cd, Cr^{III}, Cr^{VI}, Mg, Zn, Al, Mn^{II}, Cu, Mo^{VI}, Bi or W^{VI}, the limit of detection lies in the range 2 to 50 μg of V. A similar method is also described, in which a paper disc is used instead of a column. The R_F value is 1·0 and the limit of detection in this case is 5 to 200 μg of V. B. VASZKO

511. **Colorimetric determination of vanadium with tungstophosphoric acid.** Z. Gregorowicz (Inst. Inorg. Chem., Silesian Tech. High School, Gliwice, Poland). *Z. anal. Chem.*, 1960, **175** (3), 161–165 (in German).—The concn. of H_3PO_4 and of WO_4^{2-} can be varied over a wide range without affecting accuracy, but the extinction at 265 mμ decreases with increasing excess of HNO_3. *Procedure*—To the soln. of V (50 μg of V per ml) add conc. HNO_3 (2 ml), H_3PO_4 (*d* 1·72) (1 ml) and 0·25M-Na_2WO_4 (2 ml), dilute with H_2O to 15 to 20 ml and boil for 2 min. After cooling the soln., dilute to 25 ml and determine the colour on a Pulfrich photometer fitted with a S47 filter. Up to 150 mg of Fe^{3+} does not interfere. J. P. STERN

512. **Colorimetric determination of vanadium with thiocyanate.** G. S. Deshmukh and S. V. Tatwawadi (Jabalpur Univ., Benares, India). *Ann. Chim., Roma*, 1960, **50** (3–4), 428–431.—A known excess of KSCN soln. ($\simeq$ 0·1N) is added to the soln. of vanadate in an acid medium (N-H_2SO_4) at 80°. The vanadate is quant. reduced to V^{4+} according to the equation—

$$KSCN + 6H_2VO_4 + 4H_2O \rightarrow KCN + 6V(OH)_4 + H_2SO_4.$$

The blue colour of the resulting soln. is used for colorimetric micro-determination.

L. A. O'NEILL

513. **Spectrophotometric determination of vanadium with *N*-benzoyl-*N*-phenylhydroxylamine.** U. Priyadarshini and S. G. Tandon (Mahakoshal Mahavidyalaya, Jabalpur Univ., India). *Chem. & Ind.*, 1960, (29), 931–932.—*N*-Benzoyl-*N*-phenylhydroxylamine forms a violet water-insoluble complex with vanadate ions in strongly acid soln. (2N to 10N). The complex can be extracted with $CHCl_3$ and exhibits max. absorption at 490 to 510 mμ. The complex is very stable and Beer's law is obeyed over a wide range of concn. of vanadium. Large amounts of Cr^{3+}, Al^{3+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+} and Th^{4+} do not interfere; Fe^{3+} and UO_2^{2+} can be tolerated to a large extent, but Zr^{4+}, MoO_4^{2-} and Ti^{4+} interfere. The method is claimed to be more sensitive and specific than the tungstophosphate method of Wright and Mellon (*Anal. Chem.*, 1937, **9**, 251). K. A. PROCTOR

514. **Determination of vanadium tetroxide in the presence of vanadium pentoxide in kieselguhr catalysts.** K. Brotánková-Zvilská (Res. Inst. Inorg. Chem., Ústí Nad Labem, Czechoslovakia). *Chem. Prùmysl*, 1960, **10** (6), 303–304.—Quadrivalent V is titrated with permanganate, V^V is then reduced to V^{IV} and titrated again. *Procedure*—To the finely powdered sample (2 to 3 g) add H_2SO_4 (1:1) and decompose by heating gently for 30 to 45 min. Transfer the cooled product to a 250-ml flask, dilute to vol. and set aside for the SiO_2 to settle. Dilute 50 to 100 ml of this soln. with H_2O to about 400 ml, then add H_3PO_4 (*d* = 1·70) (5 ml) and after 1 min. titrate with 0·1N-$KMnO_4$ till the soln. is pink. Add $FeSO_4$ soln. (183 g of $FeSO_4.7H_2O$ plus 100 ml of H_2SO_4) (20 ml), and $(NH_4)_2S_2O_8$ soln. (20%) (10 ml) and after 2 min. titrate with 0·1N-$KMnO_4$. J. ZÝKA

515. **Determination of niobium in titanium ores and pigments.** L. A. Balchin and D. I. Williams (Laporte Titanium Ltd., Stallingborough, Lincs., England). *Analyst*, 1960, **85**, 503–508.—The finely ground sample (0·5 g $\equiv$ 2·5 mg of Nb_2O_5) is dissolved in 40% HF, the soln. is evaporated to 2 to 3 ml, cooled and transferred to a polyethylene separating-funnel with 25 ml of an acid mixture (a soln. 6M in H_2SO_4, 10M in HCl and 2·2M in NH_4F). The liquid is extracted twice according to a specified procedure with a solvent mixture (isobutyl methyl ketone equilibrated with the acid mixture). The two extracts are shaken, first separately and then together, with 10-vol. H_2O_2, the H_2O_2 extracts are evaporated to fuming and heating is continued until SO_3 and ammonium salts and organic matter are removed. The residue (mainly Nb_2O_5 and Ta_2O_5) is dissolved in 5 ml of 40% HF, H_2SO_4 (1 ml) is added and the mixture is evaporated until dense fumes of SO_3 are evolved. The cooled liquid is diluted to 25 ml with conc. HCl, placed in a polarographic cell, N or H is passed through and an a.c. polarogram is recorded against the mercury-pool electrode. The height of the peak for Nb is measured and referred to a calibration graph. Tantalum does not interfere. The accuracy of the method was confirmed by X-ray fluorescence spectroscopy. A. O. JONES

516. **Separation of niobium and tantalum by a chromatographic adsorption-complexing method.** L. S. Aleksandrova and K. V. Chmutov. *Izv. Akad. Nauk SSSR*, 1960, (5), 801–805.—Mixtures of oxalate complexes of Nb and Ta in the presence of HCl are separated on a column of activated carbon saturated with phenylarsonic acid. At 75° Ta is completely retained on the column and Nb passes into the percolate. The column (250 mm long and 12 mm in diam.), containing 10 g of activated carbon, is washed with HCl to remove Fe, then

saturated with phenylarsonic acid (2·4 g is completely adsorbed) and dried. Test soln. are prepared by fusing Nb_2O_5 and Ta_2O_5 (12·5 mg of each) with $K_2S_2O_7$, dissolving the melt in 50 ml of 4% ammonium oxalate soln. and making up to 100 ml with 4% ammonium oxalate soln. and HCl (the final soln. should be 0·65N in HCl). The test soln. is passed through the column at 95° at a rate of 40 ml per hr. Niobium passes into the percolate and Ta is eluted from the column with 7% oxalic acid soln. The absolute concn. of Nb and Ta are determined colorimetrically with pyrogallol, and the relative amounts of Nb and Ta are determined radiometrically by adding ^{95}Nb and ^{182}Ta to the initial soln. A. BURWOOD-SMITH

517. **Determination of niobium and tantalum with cinnamohydroxamic acid and *N*-cinnamoyl-*N*-phenylhydroxylamine.** A. K. Majumdar and A. K. Mukherjee (Dept. of Inorg. and Anal. Chem., Jadavpur Univ., Calcutta, India). *Anal. Chim. Acta*, 1960, **22** (6), 514–519 (in English).—Niobium and Ta are separated from other ions by pptn. with cinnamohydroxamic acid in the presence of EDTA at pH values > 5·0. The niobium complex is stable up to 225° and is weighed directly; the tantalum ppt. must be ignited to Ta_2O_5. Titanium, Zr and Mo interfere. Niobium is pptd. quantitatatively with *N*-cinnamoyl-*N*-phenylhydroxylamine from 10% (v/v) H_2SO_4 soln. and from soln. of pH up to 7·5; for Ta the acid concn. should be between 2·5 and 10% (v/v). Interference is shown by Ti^{4+}, Zr^{4+}, VO_3^-, MoO_4^{2-}, WO_4^{2-}, Fe^{3+}, Sn^{2+} and Sb^{3+}. R. M. S. HALL

518. **Determination of oxygen-18 in phosphate ion.** M. Anbar, M. Halmann and B. Silver (Weizmann Inst. of Sci., Rehovoth, Israel). *Anal. Chem.*, 1960, **32** (7), 841–842.—The procedure is based on the controlled pptn. of PO_4^{3-} (0·2 to 0·5 millimole in ≃ 5 ml of H_2O) as Ag_3PO_4 by $AgClO_4$ soln. at pH 3 to 5. The ppt. is collected, dried *in vacuo* at 60° to 70°, and then heated at 1000° for 10 min. *in vacuo*. The evolved O is measured in a mass spectrometer by scanning masses 32 to 36. The method is fast and accurate, although in the presence of interfering ions, and in the analysis of biological reaction mixtures, it is preferable to precipitate $Ba_3(PO_4)_2$, dissolve this in 2N-$HClO_4$, pass the soln. through a column of Dowex 50-X4 (H^+ form), and then precipitate Ag_3PO_4 from the percolate with $AgClO_4$. W. J. BAKER

519. **Non-aqueous colorimetric method for the determination of ozone.** A. D. Delman, A. E. Ruff, B. B. Simms and A. R. Allison (New York Naval Shipyard, N.Y.). *Advanc. Chem. Ser.*, 1959, **21**, 119–123.—A procedure for the quant. measurement of atmospheric ozone is described. The method depends on the rate of colour production on ozonisation of soln. of *N*-phenyl-2-naphthylamine in dichlorobenzene. Beer's law is obeyed, the sensitivity is ≃ $1·8 \times 10^{-3}$ mg of ozone, and reproducible results are obtained. Oxygen and oxides of nitrogen, in concn. greater than those normally occurring in the atmosphere, do not interfere. CHEM. ABSTR.

520. **Photometric determination of sulphides in baths for metal sulphiding.** F. K. Baev and L. V. Kanevskaya. *Izv. Vŭssh. Uchebn. Zavedenii, Khim. i Khim. Tekhnol.*, 1959, **2** (6), 843–845; *Ref. Zhur., Khim.*, 1960, (14), Abstr. No. 56,747.—A rapid and sufficiently accurate method is developed for the determination of S^{2-} in thiosulphate - thiocyanate baths, based on photometry of a colloidal soln. of CdS with glycerol as protective agent. To 20 ml of a soln. containing 0·5 mg of $CdSO_4$ per ml and 2 ml of glycerol add 10 to 20 ml of the test soln., dilute to 100 ml and measure the extinction with a blue filter. The CdS colloidal soln. is stable for > 1 hr. Even large amounts of $Na_2S_2O_3$ (up to 316 mg) and KSCN (up to 126 mg) do not interfere; the max. error is 4·5%. C. D. KOPKIN

521. **Potentiometric determination of sulphide ions and the behaviour of silver electrodes at extreme dilution.** M. W. Tamele, V. C. Irvine and L. B. Ryland (Emeryville Res. Center, Shell Devel. Co., Calif., U.S.A.). *Anal. Chem.*, 1960, **32** (8), 1002–1007.—In the sensitive and accurate method described, the S^{2-} are titrated with $AgNO_3$ in a soln. buffered with Na acetate and with a sulphide-coated silver electrode. Results have been obtained on the behaviour of the electrode over a wide range of S^{2-} and Ag^+ concn. K. A. PROCTOR

522. **Spectrophotometric method with 1,1′-dianthrimide for the determination of strength of concentrated sulphuric acid.** F. J. Langmyhr and O. B. Skaar (Chem. Inst. A, Univ. of Oslo, Blindern, Norway). *Anal. Chim. Acta*, 1960, **23** (1), 28–30.—The sample of H_2SO_4 (80 to 96%) is mixed with 8 ml of a 1% soln. of 1,1′-dianthrimide in 96·12% H_2SO_4 to produce a total vol. of 100 ml. The intensity of the green colour produced increases with increasing concn. of acid. The extinction at 650 mμ is determined against 96·12% H_2SO_4 as blank. For H_2SO_4 concn. in the range 96 to 99·5%, 2 ml of 1,1′-dianthrimide soln. is used. Calibration curves are prepared from a series of acid samples assayed volumetrically. H. N. S.

523. **Analysis for industry [titrimetric determination of sulphate].** A. M. G. Macdonald. *Ind. Chem.*, 1960, **36**, 345–348.—Methods based on the use of lead nitrate, 4-amino-4′-chlorodiphenyl and EDTA - Ba are reviewed and compared. (55 references.) S.C.I. ABSTR.

524. **Micro-method for the determination of sulphate by flame photometry.** G. A. Robinson (Dept. Physiol. Sci., Ontario Veterinary College, Guelph). *Canad. J. Biochem. Physiol.*, 1960, **38** (7), 643–648.—Sulphate is determined by equilibrating the $BaSO_4$ formed with an ethanol - lithium soln. and measuring the primary emission of Ba in soln. at 8500 A. *Procedure*—Equal vol. (*e.g.*, 1 ml) of test soln. are introduced into each of 6 Pyrex-glass culture tubes (10 mm × 75 mm). To tubes nos. 1, 2, 5 and 6 add 0·25 ml of HCl (0·5N); to tubes 3 and 4 add 0·25 ml of barium soln. (20 ml of a soln. containing 1·778 g of $BaCl_2.2H_2O$ per litre, and 41·4 ml of 37% HCl, diluted to 1 litre). Dry all tubes at 95°. Cool, and to tubes 3, 4, 5 and 6 add 1 ml of ethanol - lithium reagent (1·53 g of LiCl, 8·27 ml of 37% HCl and 900 ml of ethanol, diluted to 1 litre with H_2O), shake well, stopper, and store at room temp. overnight. Immediately before flame photometry, add 0·25 ml of Ba - ethanol soln. (5 ml of a soln. containing 1·778 g of $BaCl_2.2H_2O$ per litre, plus 1·53 g of LiCl, 8·27 ml of 37% HCl and 900 ml of ethanol, diluted to 1 litre with H_2O) to tubes 1 and 2. Filter if necessary. The Ba present in the soln. is then determined quant. by flame photometry at a wavelength of 8500 A. Tracings recorded for tubes 1 and 2 represent an emission of

100%, those for 5 and 6 an emission of 0%. Results for tubes 3 and 4 are referred to a standard curve prepared with $(NH_4)_2SO_4$ soln. (2 μg of sulphate per ml). Alkali metals increase the apparent Ba content, but the use of 6 tubes for each sample compensates for this. Results are given for some org. and inorg. sulphur-containing compounds. The method is suitable for determining 0·1 to 3·5 μg of sulphate, and can be adapted for larger amounts.
R. A. HENDEY

525. **Determination of the sulphate content of chromium plating solutions by a combustion method.** R. St. J. Emery (Tyseley Grp. Lab., Wilmot Breeden Ltd., Birmingham, England). *Electroplating*, 1960, **13** (7), 253–259.—The Strohlein apparatus for the determination of C and S in steel by combustion is described, and the procedure for the determination of S in steel is adapted to the analysis of chromium plating soln. Chromic acid in the sample (2 ml) is reduced to non-volatile oxides with iron and tin powders in a porcelain boat containing ignited asbestos wool and ethanol (1 ml) by heating for 1 hr. at 100°; the oxides are dried for 2 hr. at 150° and burnt in a stream of O. The SO_3 produced is absorbed in dilute H_2O_2 soln. and the SO_4^{2-} content determined by titration with 0·025N-NaOH standardised against a synthetic mixture of chromic acid soln. and H_2SO_4 similarly treated. A single analysis takes 3·5 hr., but samples can be analysed in batches of 6 to 8 with little increase in the time required. Results are compared with those obtained by the precipitation method.
C. H. COWPER-COLES

526. **The sulphur dioxide test for selenous acid.** E. R. Caley and C. L. Henderson (McPherson Chem. Lab., Ohio State Univ., Columbus, U.S.A.). *Anal. Chem.*, 1960, **32** (8), 975–978.—The maximum sensitivity of the detection of SeO_3^{2-} in H_2SO_4 soln. by reduction to Se with SO_2 is obtained in 5·5M-H_2SO_4 at 80°. Selenic acid interferes and the procedure should therefore not be used for detecting SeO_3^{2-} in SeO_4^{2-}. Hydrogen peroxide inhibits the reaction.
T. R. ANDREW

527. **Fluorimetric determination of traces of selenium.** J. H. Watkinson (Rukuhia Soil Res. Sta., Dept. of Agric., Hamilton, New Zealand). *Anal. Chem.*, 1960, **32** (8), 981–983.—The toluene soln. of selenadiazole, formed from 3,3′-diaminobenzidine by the method of Cheng (*Anal. Abstr.*, 1957, **4**, 473, 1189) shows an intense green fluorescence when irradiated at 420 mμ. The soln. is irradiated with a mercury-vapour lamp, with a filter to isolate the 405-mμ and 436-mμ lines, and the fluorescence is isolated by means of an interference filter intended for the determination of Na (589 mμ). The intensity is recorded with an IP21 photomultiplier and microammeter. A blank of ≃ 0·05 μg of Se is obtained, and as little as 0·01 μg of Se may be detected. Examples are given of the application of the method to a variety of crops and to soil.
T. R. ANDREW

528. **Liquid - liquid extraction of polonium-208 tracer from bismuth target solutions.** F. L. Moore (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1960, **32** (8), 1048–1049.—Polonium-208 may be readily extracted by 2,4-dimethylpentan-3-ol or 2,6-dimethylheptan-4-ol from soln. 6M in HCl and < M in HNO_3. The efficiency is > 98% compared with the 90% attained by co-pptn. on LaF_3.
T. R. ANDREW

529. **Colorimetric micro-determination of sexavalent chromium.** G. Halliwell (Rowett Res. Inst., Aberdeen, Scotland). *Anal. Chem.*, 1960, **32** (8), 1041–1042.—The method is based on the oxidation of a stable colourless CdI_2 - starch reagent by Cr^{VI} to the blue starch - iodide complex. The concn. range is 0·05 to 0·5 μg of Cr per ml in a final vol. of 10 ml. Recoveries ranged from 96 to 100% when the method was applied to samples of a fermentation medium.
G. P. COOK

530. **The extractability of tungsten(VI) thiocyanate. Experiments with radio-tungsten.** V. Pfeifer (Anal. Inst., Univ., Vienna, Austria). *Mikrochim. Acta*, 1960, (4), 518–533 (in German).—The W - SCN^- complex is extractable by organic solvents, preferably amyl alcohol (**I**) and readily separated from other elements. Fluoride and Fe^{III} interfere, and since Mo is extracted with the W it must be removed. The W is determined photometrically (470 mμ) by the quinol method. The following procedure, based on the results of an investigation with the radioactive isotope ^{185}W, is recommended. The accuracy on 1 μg is within ± 3%. *Procedure*—Dissolve 1 g of sample in 4 to 6N-HCl (20 to 100 ml). Extract an aliquot (≯ 1 mg of W) with isopropyl ether to remove $FeCl_3$. Add 20% ascorbic acid (5ml), 5N-KSCN (5 ml) and 6N-HCl to 50 ml. Extract twice with **I** - $CHCl_3$ (1:1) (10 ml) and then with **I** (20 ml), and re-extract the organic phase with a little 4N-HCl. Add light petroleum (20 ml) and extract with three or four 15-ml portions of aq. NH_3 (3% w/v) and evaporate to dryness. Destroy the SCN^- with $HClO_4$ and remove H_2SO_4 by fuming. To remove Mo, extract a weakly acidic soln. with potassium ethylxanthate and $CHCl_3$, and remove organic matter from the aq. phase. Evaporate to 1 to 2 ml. Add 10% quinol in conc. H_2SO_4 (5 ml) and compare the extinction at 470 mμ with a calibration curve.
J. P. STERN

531. **3-Hydroxyiminomethylsalicylic acid as an analytical reagent. II. Spectrophotometric determination of uranium.** Asit Kumar Ray and Priyadaranjan Rây. *J. Indian Chem. Soc.*, 1960, **37** (3), 141–145.—Quadrivalent U gives an orange - red colour with 3-hydroxyiminomethylsalicylic acid in alkaline soln., the extinction of which is measured at 400 mμ. The optimum pH is 6·7 to 9·3 with an excess of the reagent (5 to 6 times the molar proportion of U) for the max. development of colour. The colour is stable at temp. < 30°. Beer's law is obeyed in the range 7 to 119 p.p.m. of U. The sensitivity is 0·12 μg of U per ml. Most cations and anions interfere, and separation is essential. The composition (1:1) of the coloured complex is evaluated by Job's method and a probable constitution is suggested.
I. JONES

532. **Spectrophotometric determination of uranium with benzohydroxamic acid in n-hexanol.** C. E. Meloan, P. Holkeboer and W. W. Brandt (Dept. of Chem., Purdue Univ., Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 791–793.—The method, applicable to 0·2 to 12 mg of U, is based on formation of the coloured U^{6+} - benzohydroxamic acid complex in aq. soln. at pH 6·2 and its extraction into n-hexanol (**I**). *Procedure*—To the sample soln. (containing ≯ 5×10^{-5} mole of U^{6+}) add 0·1M-benzohydroxamic acid (10 ml), dilute to between 50 and 100 ml with H_2O and adjust the pH to 6·2 ± 0·1 with 0·3M-NaOH. Extract the complex into 25 ml of **I** (centrifuging

if necessary) and measure the extinction at 380 mμ in a 1-cm cell against **I**. Beer's law holds for 7×10^{-7} to 2×10^{-5} mole of UO_2^{2+} in 10 ml of **I**. The method is sensitive and accurate, but strong oxidising and reducing agents and Al, Sn^{4+}, Zr^{4+} and Ti^{4+} interfere seriously. By increasing the concn. of the reagent, interference by Th^{4+}, Ce^{4+}, W and Mo can be diminished or eliminated. The effects of the reagent to U ratio, pH, different ions, extraction interferences and reagent stability are discussed. W. J. BAKER

533. **Polarography of uranium in thiocyanate medium.** S. C. Saraiya, V. S. Srinivasan and A. K. Sundaram (Atomic Energy Est. Trombay, Bombay, India). *Anal. Chim. Acta*, 1960, **23** (1), 77–82.—Uranyl ions in thiocyanate soln. give two polarographic waves, corresponding to $UO_2^{2+} \rightarrow U^{4+}$ and $U^{4+} \rightarrow U^{3+}$, respectively. The influence on these waves of thiocyanate and acid ($HClO_4$) concn., temp., and capillary dimensions is studied. H. N. S.

534. **Polarographic determination of uranium and its separation by solvent extraction in the presence of phosphate.** H. Menke and G. Herrmann (Inst. f. Anorg. Chem., Univ., Mainz, W. Germany). *Z. anal. Chem.*, 1960, **175** (5), 324–337.—Attempts to reproduce the work of Hecht *et al.* (*Anal. Abstr.*, 1957, **4**, 99) with the catalytic nitrogen wave gave unsatisfactory results, but 5 μg to 5 mg of U per ml was successfully determined by the method of Legge (*Anal. Abstr.*, 1955, **2**, 624), in which the basal electrolyte consists of 0·9M-H_2SO_4, 0·5M-oxalic acid, 0·015% of gelatin and 0·1% (v/v) of conc. HCl. The determination of 10 to 100 μg of U by polarography after extraction with non-aq. solvents is reported. The separation of U from phosphate soln. is hindered by complex formation. Quantitative results are reported for the extraction of U into tri-n-butyl phosphate, with Al or Fe^{III} as complexing agent. E. G. CUMMINS

535. **Errors in the titrimetric determination of uranium-235.** J. Rynasiewicz, R. F. Dufour and D. P. Stricos (Knolls Atomic Power Lab., General Electric Co., Schenectady, N.Y.). *Anal. Chem.*, 1960, **32** (8), 1048.—When ^{235}U is assayed by reduction to U^{IV} and titration to U^{VI} low recoveries are obtained. The procedure is satisfactory for natural uranium and it is suggested that the U^{IV} is oxidised by atmospheric O to U^{VI} under the influence of the α- and γ- radiation emitted by the active material. T. R. ANDREW

536. **Analytical method for the precise determination of uranium in pure uranyl nitrate solutions.** U.K.A.E.A. (Production Group, Operations Branch, Springfields, Lancs., England). U.K.A.E.A. Report PG 133 (S), 1960. 6 pp.—Full details are given of a procedure in which the U is pptd. by the addition of aq. NH_3 and then ignited to U_3O_8, which is weighed. In the analysis of soln. with a content of U of 20% (w/v) the standard deviation is $\simeq \pm$ 0·02%. G. J. HUNTER

537. **Analytical method for the absorptiometric determination of uranium in impure liquors containing less than 2% of uranium.** U.K.A.E.A. (Production Group, Operations Branch, Springfields, Lancs., England). U.K.A.E.A. Report PG 132 (S), 1960. 7 pp.—Full details of the procedure are given. The U is extracted from a soln. containing HNO_3 into ethyl ether. After the removal of the ether and the destruction of organic matter the residue is dissolved in H_2SO_4; the soln. is neutralised with NaOH, and Na_2CO_3 and $Na_4P_4O_7$ are added; the extinction is measured at this stage and again after the addition of H_2O_2. The content of U is derived from the difference between the extinctions by means of a calibration graph. The coefficient of variation is $\simeq$ 1·7%. G. J. HUNTER

538. **Analytical method for the gravimetric determination of uranium in impure liquors and solid residues containing more than 2% of uranium.** U.K.A.E.A., (Production Group, Operations Branch, Springfields, Lancs., England). U.K.A.E.A. Report PG 129 (S), 1960. 13 pp.—Liquors are evaporated and the residue is dissolved in $Ca(NO_3)_2.4H_2O$-HNO_3, from which U is extracted into ethyl ether containing HNO_3 by elution from a cellulose column. The ether is removed by distillation and the ppt. produced by the addition of aq. NH_3 is ignited to U_3O_8, which is weighed. Solid samples are treated with acids, and possibly by a fusion process, to destroy organic matter and to ensure a high recovery of the U in HNO_3 soln., which may be treated like a liquor. For liquors with a concn. of U of 30% (w/v) the standard deviation is $\simeq \pm$ 0·17%. G. J. HUNTER

539. **Analytical method for the determination of uranium in Springfields effluents and contributory discharges.** U.K.A.E.A. (Production Group, Operations Branch, Springfields, Lancs., England). U.K.A.E.A. Report PG 130 (S), 1960. 14 pp.—Full details are given of the procedure, in which the sample (500 ml) is evaporated and the U is converted into $UO_2(NO_3)_2$, which is purified by extraction into ethyl ether. The ether having been removed, H_2O_2 is added and the U is determined absorptiometrically. For soln. with contents of U of > 5 μg per ml the coefficient of variation is $\simeq$ 3%. G. J. HUNTER

540. **Analytical method for the general gravimetric determination of uranium in ores and concentrates.** U.K.A.E.A. (Production Group, Operations Branch, Springfields, Lancs., England). U.K.A.E.A. Report PG 128 (S), 1960. 9 pp.—Full details of the procedure are given. The sample (5 g) is dissolved in HNO_3 and the soln. is evaporated to dryness. The residue is dissolved in a mixture of $Ca(NO_3)_2.4H_2O$, $Fe(NO_3)_3.9H_2O$ and HNO_3 and transferred to a cellulose - alumina column, and the U is eluted with ethyl ether containing HNO_3, which is then removed by distillation from water. The U is then pptd. by adding aq. HN_3 and the ppt. is ignited to U_3O_8, which is weighed. For ores with contents of U from 82% to 93% the standard deviation is $\simeq \pm$ 0·08%. G. J. HUNTER

541. **Analytical method for the absorptiometric determination of uranium in solid residues from ore dissolving.** U.K.A.E.A. (Production Group, Operations Branch, Springfields, Lancs., England). U.K.A.E.A. Report PG 131 (S), 1960. 7 pp.—Full details of the procedure are given. The dried sample (2 g) is treated with HF and HNO_3 and the U is then extracted into ethyl ether. After removal of the ether and destruction of any organic matter with $HClO_4$ - HNO_3, the U is determined absorptiometrically in a soln. containing Na_2CO_3, $Na_2P_4O_7$ and H_2O_2. The coefficient of variation is 0·17%. G. J. HUNTER

542. **Removal of molybdenum in analysis of uranyl and other phosphates.** A. H. Volborth (Mining Anal. Lab., Univ. Nevada, Reno, U.S.A.). *Anal. Chem.*, 1960, **32** (7), 882–883.—The H_2S method previously described (*Z. anorg. Chem.*, 1954, **276**, 159) has been adapted for the more rapid complete analysis, with a smaller sample, of complex phosphates, *e.g.*, autunite. After dissolution of the sample, all the P is pptd. as ammonium molybdophosphate from HNO_3 soln.; the remainder of the Mo in the filtrate is then pptd. as MoS_3 (after destruction of NO_3^-) leaving all the cations in soln. for complete analysis. The analyses reported (including that of meta-autunite) show that the accuracy is high. Double pptn. are necessary if H_2SO_4 is used in the dissolution stage.
W. J. BAKER

543. **Analytical application of embelin. I. Estimation of uranium and thorium and their separation.** C. H. Bheemasankara Rao and V. Venkateswarlu (Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1960, **175** (2), 114–117 (in English).—With embelin (2,5-dihydroxy-3-undecyl-1,4-benzoquinone) (**I**), uranium soln. at pH 6·0 to 6·5 give violet-tinted complexes that are soluble in ethanol, while Th is pptd. in 0·4N-HCl as a violet complex that is insoluble in ethanol. This difference in the conditions of pptn. has been made use of for the separation of Th from U and rare-earth elements. *Procedure for the separation of Th from U*—To a soln. of the nitrates of U and Th is added enough HCl to maintain the acidity at 0·3 to 0·4N, the soln. is diluted to 200 ml, warmed to $\simeq 60°$ and **I** soln. (1% in acetic acid) is added dropwise (25 ml for each 0·1 g of ThO_2), with stirring. The mixture is digested on a steam bath for $\simeq$ 15 min. The ppt. is allowed to settle, collected on Whatman No. 41 paper, washed with NH_4NO_3 soln. and then ignited in a platinum crucible and weighed as ThO_2. When the ThO_2 is pale yellow, a second pptn. is recommended. Uranium is determined in the filtrate by using **I** soln. at pH 6·0 to 6·5. The ppt. is filtered off, washed with ammonium acetate soln. and finally ignited and weighed as U_3O_8. No interference is caused in 0·1 to 0·4N-HCl by Cu, Cd, Ca, Ba, Sr, Mn, Mg, Al, Be or Zn, but Ti, Zr and Fe^{3+}, interfere.
B. B. BAUMINGER

544. **Analysis of naturally leached uranium-thorium ore samples. Application of pure gamma-spectrometry.** P. W. De Lange (Radioactivity Div., Nat. Phys. Res. Lab., Pretoria, S. Africa). *Anal. Chem.*, 1960, **32** (8), 1013–1017.—Various radiometric procedures are examined and the possible errors summarised. A γ-spectrometric method that gives results comparable to those of other radiometric, chemical and mass-spectrometric methods is described.
K. A. PROCTOR

545. **Determination of uranium and thorium in their compounds by γ-radiation measurements.** A. F. Korvezee. *Rec. Trav. Chim. Pays-Bas*, 1960, **79** (6), 617–621 (in English).—The radiometric determination of uranium and thorium in their compounds can be effected in principle by γ-counting with a scintillation spectrometer. The complications that arise when the radioactive equilibrium with the daughter products in the samples to be analysed is not established are discussed.
J. M. JACOBS

546. **Polarographic determination of uranium and molybdenum in presence of each other.** G. S. Deshmukh and J. P. Srivastava (Benares Hindu Univ., Varanasi, India). *Z. anal. Chem.*, 1960, **176** (1), 28–34 (in English).—When reduced to their quinquevalent state, U and Mo can be determined simultaneously. Hydrazine sulphate acts as reductant and supporting electrolyte. *Procedure*—The sample in HCl (3 to 4M) is reduced with hydrazine hydrochloride until the soln. is brownish red. The hydrazine content of the soln. is raised to $\simeq$ 0·16M with respect to hydrazine sulphate and the pH is adjusted to 1·0. The soln. is then polarographed, and the concn. of U and Mo are obtained from the individual calibration curves. The values of $E_{\frac{1}{2}}$ *vs.* the S.C.E. are $\simeq$ − 0·23 V for U and − 0·54 V for Mo.
J. H. WATON

547. **Quantitative radiochemical analysis by ion exchange. Uranium and tellurium.** L. Wish (U.S. Naval Radiological Defense Lab., San Francisco, Calif., U.S.A.). *Anal. Chem.*, 1960, **32** (8), 920–922.—In the method described for the separation of U and Te, a soln. of a fission-product mixture in 0·1N-H_3PO_4 is loaded on to a column of Dowex-2 phosphate and eluted with H_3PO_4 soln. Tellurium is not adsorbed and, after converting the column to the chloride form, U can be quant. eluted with HCl - HF.
K. A. PROCTOR

548. **Spectrophotometric determination of traces of boron in uranium.** Hiroshi Onishi, Nasumi Ishiwatari and Hitoshi Nagai (Japan Atomic Energy Res. Inst., Tokai, Ibaraki-ken). *Bull. Chem. Soc. Japan*, 1960, **33** (6), 830–835.—The spectrophotometric determination of 0·1 to 1 p.p.m. of B in uranium (metal, U_3O_8 and uranyl sulphate) is described. The uranium metal is converted into U_3O_8, and the oxide is dissolved in H_2SO_4 and H_2O_2. Boron is separated by distillation as methyl borate from the H_2SO_4 soln., and finally determined by the curcumin method.
I. JONES

549. **Radiochemical determination of radium in uranium milling process samples.** H. G. Petrow, O. A. Nietzel and M. A. DeSesa (Raw Materials Devel. Lab., National Lead Co., Inc., Winchester, Mass., U.S.A.). *Anal. Chem.*, 1960, **32** (8), 926–927.—In the carrier-free method described, Ra is carried on $PbSO_4$, which is converted into the carbonate. The ppt. is dissolved in HNO_3, and Pb and Ra are selectively re-pptd. with fuming HNO_3. After dissolution of this ppt., Pb and Ra are separated by ion exchange and the Ra is measured by α-counting.
K. A. PROCTOR

550. **Use of phenylarsonic acid for the separation of neptunium and plutonium.** I. E. Starik, A. P. Ratner, M. A. Pasvik and F. L. Ginzburg. *Radiokhimiya*, 1959, **1** (5), 545–547; *Ref. Zhur., Khim.*, 1960, (8), Abstr. No. 30,415.—The method is based on co-pptn. of Np^{IV} with Zr phenylarsonate; Pu^{III} remains in soln. Add Zr as carrier (3 to 4 mg of Zr for each 10 ml of soln.) to the soln. of Np and Pu in N-HCl, then an excess of hydroxylamine to reduce Np and Pu, and heat on the water bath for 2·5 hr.; add twice the vol. of 4% phenylarsonic acid soln. Centrifuge and wash the ppt. with 1% HCl, treat it, with slight warming, with 5% NaOH soln. and dissolve it in HCl. The soln. contains Np and Zr. To the first filtrate add La as carrier (2 mg of La for 10 ml of soln.), evaporate the soln. on a water bath almost to dryness, treat with acid and precipitate $La(OH)_3$, which carries down the Pu. Recoveries are about 95% for the Np and up to 97% for the Pu.
C. D. KOPKIN

551. **Determination of protactinium-233 in irradiated thorium.** J. J. McCormack, F. H. Cripps and W. A. Wiblin (Atomic Weapons Res. Estab., Aldermaston, Berks., England). *Anal. Chim. Acta*, 1960, **22** (5), 408–413.—Uranium-233 is assessed as its precursor ^{233}Pa by β-counting, 1-g portions of irradiated thorium metal being treated to separate 200 to 10^5 disintegrations per min. of ^{233}Pa. The chemical yield is found from the recovery of ^{231}Pa tracer added to the original soln. The soln. (in HNO_3 - HF) of thorium metal, with added ^{231}Pa, is extracted with 2,4-dimethylpentan-3-ol, and the Pa is back-extracted and adsorbed on a CG-400 ion-exchange column. The Pa is eluted, with 11N-HCl - 0·5N-HF and evaporated on to a stainless-steel disc for counting. An end-window counter is used for β-counting and calibrated with a standard ^{237}Np - ^{233}Pa source. The tracer ^{231}Pa is determined by α-counting, giving the chemical yield of ^{233}Pa and the correction to the β-count for the γ-emission from the ^{231}Pa. The yield is 70 to 80%. With synthetic mixtures of the Pa isotopes the ratio found to the ratio added is 0·990 ± 0·024 (six determinations). R. M. S. HALL

552. **Spectrophotometric determination of fluoride with thorium chloranilate.** A. L. Hensley and J. E. Barney, jun. (Standard Oil Co., Whiting, Ind., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 828–831.—Less than 10 mg of F^- per 60 ml of soln. can be determined to within ≃1·3% by measuring the extinction of the complex formed with thorium chloranilate in buffered aq. 2-methoxyethanol at pH 4·5 and 25°. The measurements are made in 1-cm cells at 540 mμ in 2-methoxyethanol - H_2O (1:3) for F^- concn. of 0·2 to 10 mg, and at 330 mμ in 2-methoxyethanol - H_2O (1:9) for concn. < 0·2 mg, two separate calibration curves being required. Interfering ions must be removed initially with ion-exchange resin, or (if Al, Zr, PO_4^{3-}, MoO_3^-, citrate or tartrate is present) the F^- should be separated by steam-distillation. The sensitivity (limit of detection is 0·01 p.p.m.) is equal to that of the usual colorimetric methods based on the bleaching action of F^-, and frequent re-calibration is unnecessary. A result can be obtained in ≃ 1 hr.
W. J. BAKER

553. **Zirconyl - alizarin chelate in spectrophotometric determination of trace amounts of fluorine.** R. P. Ashley (Aluminium Lab., Ltd., Arvida, Que., Canada). *Anal. Chem.*, 1960, **32** (7), 834–836.—Errors in the Th - alizarin photometric procedure of Willard and Winter (*Ind. Eng. Chem. Anal. Ed.*, 1933, **5**, 7) caused by free acid in the steam-distillate can be avoided by the use of a Zr - Na alizarin-sulphonate reagent (**I**), the complex of which is also bleached by F^-. *Procedure*—To an aliquot of the distillate containing > 180 μg of F^- add 5 ml of **I** and dilute to 100 ml with H_2O; after 2·5 hr. measure the extinction in a 5-cm cell at 520 mμ against H_2O. The concn. of F^- is obtained by reference to the linear working curve. Beer's law is followed for 0 to 1·9 μg of F^- per ml; no adjustment of pH is necessary as the accuracy is unaffected at values between 0·7 and 2·9. The standard deviation of the difference between 23 results by this method and results by the Th - alizarin method (ranging from 1·5 to 88·5 μg of F^-) is 2·6 μg. Phosphates interfere. **I** is prepared by mixing 440 ml of H_2SO_4 (1:10) with 120 ml of conc. HCl and then adding 100 ml each of 0·3% aq. $ZrOCl_2.8H_2O$ soln. and 0·35% aq. Na alizarinsulphonate soln.; the mixture is filtered and diluted to 1 litre with H_2O.
W. J. BAKER

554. **Radiometric extraction method for fluoride. Pyrolysis - ion-exchange separation.** W. J. Maeck, G. L. Booman, M. C. Elliott and J. E. Rein (Atomic Energy Div., Phillips Petroleum Co., Idaho Falls, U.S.A.). *Anal. Chem.*, 1960, **32** (8), 922–925.—In the method described, the sample, after preliminary treatment by ion exchange or pyrolysis to remove interfering ions, is added to a soln. containing traces of ^{181}Hf. Trioctylphosphine is added and a liquid - liquid extraction is carried out. The Hf retained in the aq. phase is measured by γ-counting, and an inverse linear response has been established for Hf extraction *vs.* fluoride concn. At the 250-μmole level of fluoride concn., the coeff. of variation for the over-all procedure is 3·3%. K. A. PROCTOR

555. **Pyrohydrolytic separation of fluorides from catalysts by use of an oxy-hydrogen burner.** D. C. Hoel, D. T. Fanale and R. O. Clark (Gulf Res. and Development Co., Pittsburgh, Pa., U.S.A.). *Anal. Chim. Acta*, 1960, **23** (1), 83–88.—The Wickbold oxy-hydrogen burner (*cf. Angew. Chem.*, 1957, **69**, 530) is adapted to provide a combined source of heat and water vapour for the pyrohydrolysis of fluorides in catalysts for petroleum technology. Decomposition occurs in < 5 min. at ≃ 1400° and the HF is absorbed in 0·1N-NaOH and determined by the method of Megregian (*cf. Anal. Abstr.*, 1954, **1**, 2676). In the range 0·3 to 3% of F the standard deviation is > 0·04%. H. N. S.

556. **Analysis for industry.** A. M. G. Macdonald. *Ind. Chem.*, 1960, **36**, 241–243.—Colorimetric methods for the determination of chloride are reviewed. It is considered that the $Hg(SCN)_2$ and the $FeCl_3$ complex methods are the most suitable for routine use as the conditions are not critical and the methods not unduly sensitive to interference. (18 references.) S.C.I. ABSTR.

557. **Direct colorimetric determination of trace amounts of chloride.** T. Nash (Medical Res. Council, Group for Res. on Atmospheric Pollution, St. Bartholomew's Hospital, London). *Analyst*, 1960, **85**, 515.—Fluorescein shows solubility and spectral-absorption minima at the isoelectric point (*J. Phys. Chem.*, 1958, **62**, 1574). The dye, or one of its derivatives, might therefore have a strong affinity for some nascent ppt. with the likelihood of a measurable change in colour. This was realised with dibromofluorescein at pH 3·4 in the presence of AgCl below the turbidimetric level. *Procedure*—To 6 ml of the sample soln. add 0·4 ml of a 0·01% soln. of dibromofluorescein in 0·001M-alkali and 0·4 ml of 1% (v/v) acetic acid. Successively add 1, 2 and 4 drops of a 0·34% soln. of $AgNO_3$ and measure the colour of the liquid at 550 mμ, or with the use of a green filter, at 30-sec. or 1-min. intervals after the addition of dibromofluorescein. The method is applicable only to neutral unbuffered soln. containing no colloids or ions (other than Cl^-) that form insoluble silver salts, and its range is from 0 to 5 p.p.m. Up to 0·2% of SO_4^{2-} or NO_3^- can be tolerated. Samples from bubblers through which air has been passed must be boiled to remove SO_2.
A. O. JONES

558. **New quantitative chromatographic determination of chloride ion.** F. Baykut and S. Özeriş (II Chem. Inst., Univ. Istanbul). *Istanbul Univ.*

Fac. Mecmuasi, 1959, **24** (1–2), 79–82 (in German).—The chloride is chromatographed as the AgCl - NH_3 complex on S. & S. paper No. 2043 at 20° by the ascending technique with 1·16% aq. NH_3 - methanol - isopropyl alcohol (3:2:5) as solvent. Standard soln. (1 to 5 μg of Cl^- per ml) are prepared by dissolving freshly pptd. dry AgCl in 10% aq. NH_3; 1-ml aliquots are placed on the paper and developed for 5 hr. and the paper is then dried for 1 hr. at room temp. All these operations are carried out in weak red light. The spots are revealed by exposure to u.v. light as regular brown ellipses, the areas and distances of the middle points from the origin depending on the concn. of AgCl. A plot of area of spot (sq. mm) *vs.* log concn. of Cl^- (μg) yields a straight line. R. E. E.

559. **The influence of tri(hydroxymethyl)methylamine [2-amino-2-hydroxymethylpropane-1,3-diol] and of monomethyl di(hydroxymethyl)methylamine [2-methylaminopropane-1,3-diol] on mercurimetric chloride determinations.** W. Björk and I. Svensson (Inst. of Biochem., Univ. of Uppsala, Sweden). *J. Chromatography*, 1960, **4** (1), 88–91 (in English).—A quantitative study is made of the effect of these buffers on mercurimetric titrations of 0·01M-NaCl at different end-point pH values. It is shown that, at a pH higher than 2·3, 2-amino-2-hydroxymethylpropane-1,3-diol alone will remove Hg^{2+} from solution, and this effect increases with increasing pH. A larger amount of 2-methylaminopropane-1,3-diol is required to produce the same effect. E. C. Butterworth

560. **Determination of chloride and iodide in presence of each other.** A. de Sousa (Fac. of Sci., Univ. of Lisbon, Portugal). *Chemist Analyst*, 1960, **49** (2), 45.—The halides are pptd. as the silver salts from two equal samples. One of the ppt. is oxidised with $K_2Cr_2O_7$ and filtered. The $AgIO_3$ in the filtrate is reduced to AgI by means of Na_2SO_3 and filtered off. Both ppt. are dissolved in $KNi(CN)_4$ soln. and titrated with EDTA, with murexide as indicator, to determine AgI and AgI plus AgCl. If Br^- are present, the filtrate from the pptn. of AgI is treated with I^-, and the pptd. AgI is dissolved and titrated as described above, giving the Cl^- plus Br^- present in the original soln. The error in the determination of I^- is $< 1\%$. G. Burger

561. **Determination of small amounts of bromide in presence of mercuric ions.** H. J. V. Tyrrell and B. A. Dowson (Dept. of Chem., The Univ., Sheffield, England). *Analyst*, 1960, **85**, 528–529.—The method of Cunningham *et al.* for the determination of micro amounts of Cl^- (*J. Biol. Chem.*, 1941, **139**, 11) was applied to the determination of Br^-, but it was necessary to replace the silver-wire electrode by an ammonium nitrate - agar bridge leading to an external calomel reference electrode. In the presence of Hg^{2+}, a preliminary separation of the Hg was essential. Soln. of NaBr in N-$HClO_4$ and of $Hg(ClO_4)_2$ in N-$HClO_4$ were mixed to give a soln. of known molality in Br^- (2×10^{-4} to 5×10^{-4}) and with a Br^- to Hg^{2+} ratio of $\simeq 2$. The soln. (10 ml) was shaken with dithizone in $CHCl_3$ containing 1% of 6N-acetic acid. After separation of the aq. layer and washing it with $CHCl_3$, a weighed aliquot was analysed by adding $AgNO_3$ (0·0671N and 0·0255N were used) from a 0·1-ml ultra-micro burette. The end-point, indicated by a sudden change in the e.m.f. of the electrode system, was sharp, and the Br^- concn. so determined accurate. A. O. Jones

562. **Determination of periodate by the formaldehyde formed on oxidation of ethanediol.** L. Maros, I. Molnár-Perl and E. Schulek (Inst. Inorg. and Anal. Chem., L. Eötvös Univ., Budapest). *Acta Chim. Acad. Sci. Hung.*, 1960, **22** (4), 475–478 (in German).—The formaldehyde produced by the reaction of an acid soln. of IO_4^- with ethanediol is measured by its reaction with Na_2SO_3 soln., the excess of which is determined iodimetrically in the presence of KCN. By this procedure the equiv. wt. is one quarter of the mol. wt. The error is ± 0·3%. G. P. Cook

563. **Polarographic determination of manganese.** H. A. Catherino and L. Meites (Polytech. Inst. of Brooklyn, N.Y., U.S.A.). *Anal. Chim. Acta*, 1960, **23** (1), 57–65.—The method depends upon the measurement of the diffusion current of the anodic wave of Mn^{2+} in a NaOH - Na tartrate supporting electrolyte. Preliminary treatment consists of electrolyses at controlled potentials in order to convert Mn quant. into Mn^{2+} and to remove interfering elements or render them innocuous. Manganese is determined in samples containing Cu, Zn, Al, Sn, Fe, Pb, Ni, Si, As, Sb, Ag, Cr, Mo, V, C, P and S. H. N. S.

564. **Influence of metal ions and sample acidity on the determination of manganese. A study of the Lingane - Karplus method.** W. G. Scribner (Res. and Engng Div., Monsanto Chemical Co., Dayton, Ohio, U.S.A.). *Anal. Chem.*, 1960, **32** (8), 966–969.—In the application of the Lingane and Karplus method (*Brit. Abstr. C*, 1946, 153) to initially highly acid soln., the formation of a violet colour has been observed during adjustment of the soln., containing pyrophosphate, to pH 6 or 7 with NaOH. The titration, however, is correct for pure soln. of Mn, and this phenomenon has been explained as oxidation of some Mn^{II} to Mn^{III} by O from the air, with formation of equivalent H_2O_2, which is subsequently titrated with $KMnO_4$. Similar behaviour is reported in the presence of Zn, Ca, Mg or Al, but in the presence of Cu, Co or Fe the O is reduced to H_2O, and results for Mn can be seriously low (up to 60% for 0·15 millimole of Mn and 4 millimoles of Co). This error can be eliminated by carrying out the neutralisation under N. No error is reported for weakly acid sample soln. A "strongly acid" soln. is defined as one that, when added to the pyrophosphate soln., gives a pH of 1 to 2. T. R. Andrew

565. **Influence of chromium(III) on the determination of manganese. A study of the Lingane - Karplus method.** W. G. Scribner (Res. and Engng Div., Monsanto Chemical Co., Dayton, Ohio, U.S.A.). *Anal. Chem.*, 1960, **32** (8), 970–972.—In the presence of Mn^{II}, Cr^{III} may be oxidised to CrO_4^{2-} by $KMnO_4$ in the Lingane and Karplus method (*Brit. Abstr. C*, 1946, 153) and cause high results. If the pyrophosphate soln. is allowed to stand for 50 to 60 min. at pH 7 to 7·5 before being titrated, a stable chromium pyrophosphate is formed, which does not interfere. In the absence of Mn^{II} no titration of Cr^{III} takes place. T. R. Andrew

566. **Polarographic determination of technetium and ruthenium radionuclides in fission products.** D. L. Love and A. E. Greendale (Chem. Technol. Div., Naval Radiological Defense Lab., San Francisco, U.S.A.). *Anal. Chem.*, 1960, **32** (7), 780–786.—A quant. determination of ^{99m}Tc, ^{103}Ru and

^{106}Ru in fission-product mixtures can be rapidly made by selective reduction of a known fraction of the sample at the dropping-mercury electrode to an oxidation state sol. in Hg. The supporting electrolyte is M-Na citrate - 0·1M-NaOH, the applied voltage is −1·55 V *vs.* the S.C.E., the drop time is 4 sec., and the time of reduction 3 min. The amalgam is extracted from the soln. into CCl_4 (which is then removed) and the radionuclides in an HNO_3 soln. of the amalgam are then assayed by a γ-count with the NaI(Tl) crystal well-counter. The separated Ru activities are counted after ^{99m}Tc has decayed out. For ^{99m}Tc the precision is within ≃ 1%, and the accuracy is within ≃ 2% as compared with the radiochemical (^{99}Mo) procedure. Because the count rate is low and some Ru in the amalgam is sol. in H_2O and CCl_4, the precision and accuracy for ^{103}Ru and ^{106}Ru are not as high as for ^{99m}Tc. The decontamination factor from other fission products is ≃ 10^5; 50 analyses can be completed in a day by two people. Interfering radionuclides, electrode reactions for the reduction of ^{99m}Tc, and the variables in the procedure are discussed. W. J. BAKER

567. **Oxidation with potassium permanganate in the presence of fluoride. IV. Determination of ferrous iron in presence of fluoride ions.** I. M. Issa and M. Hamdy (Fac. of Sci., Cairo Univ., Egypt). *Z. anal. Chem.*, 1960, **175** (2), 110–113 (in English).—It is shown that Fe^{2+} can be determined in the presence of F^- by the use of an excess of $KMnO_4$ in alkaline medium. The excess of $KMnO_4$ is reduced by an excess of $Hg_2(NO_3)_2$ soln. and the unchanged Hg_2^{2+} are titrated with $KMnO_4$ soln. until the appearance of a pink - violet colour which persists for ≃ 40 sec. The effects of alkalinity, Fe^{2+} and F^- concn. have been studied, and the results are discussed. B. B. BAUMINGER

568. **Spectrophotometric determination of iron with 3-hydroxy-3-phenyl-1-*p*-sulphophenyltriazen.** H. K. L. Gupta and N. C. Sogani (Chem. Dept., Gov. Coll., Ajmer). *J. Indian Chem. Soc.*, 1960, **37** (2), 97–100.—Tervalent Fe forms a bluish-black water-soluble complex with 3-hydroxy-3-phenyl-1-*p*-sulphophenyltriazen in the pH range 2·0 to 4·3, with absorption peaks at 520 and 650 mμ; full colour development is attained at a ratio of Fe to reagent of 1:15. The system obeys Beer's law in the range of 1 to 20 p.p.m. of Fe. The molecular extinction coeff. of the complex at 650 mμ is $4·47 \times 10^3$. With visual comparison in Nessler cylinders, the sensitivity is 1 part of Fe in 5×10^6 parts of soln.; the spot-plate identification limit is 0·1 μg of Fe in 0·15 ml of soln. I. JONES

569. **Determination of iron in brass with tiron.** B. Lehký (Kovohutě Povrly, Czechoslovakia). *Hutn. Listy*, 1960, **15** (7), 554–555.—*Procedure*—Dissolve the finely divided sample (0·4 g) in HCl (1:4) (20 ml) and H_2O_2 (30%) (2 ml), remove the excess of H_2O_2 by boiling, cool, dilute with H_2O to 200 ml and mix. To 10 ml add aq. NH_3 till the soln. is blue and decolorise dropwise with HCl. Add a buffer soln. of pH 9·5 (71·6 g of Na_2HPO_4 and 4 ml of N-NaOH in 1 litre of H_2O) and 5M-KCN (0·1 to 0·4 ml) for masking Cu, then add tiron soln. (1 ml) and dilute with H_2O to 50 ml. Mix, and after 15 min. measure the extinction in a Pulfrich photometer with a S50 filter. Good results were obtained with samples containing 0·05 to 0·6% of Fe. The presence of Zn, Pb and Sn causes no interference. Oxidising agents must be removed. J. ZÝKA

570. **Studies on the metal complexes of hydroxamic acids. V. Co-determination of iron and manganese with aminobenzohydroxamic acid.** R. L. Dutta (Inorg. Chem. Lab., Indian Ass. for the Cult. of Sci., Calcutta). *J. Indian Chem. Soc.*, 1960, **37** (3), 167–170.—The co-determination of Fe and Mn with 2-aminobenzohydroxamic acid as a colorimetric reagent is studied. Either Fe^{3+} or Fe^{2+} are determined by measuring the extinction of the orange - red complex (absorption max. at 450 mμ) extracted from aq. medium at pH 4·5 with isobutyl alcohol; Mn is then determined in the aq. layer with the same reagent at a pH > 9·2, when a wine-red complex (absorption max. at 490 to 500 mμ) is formed. Amounts of Fe 250 times that of Mn can be determined. I. JONES

571. **Electron analysis of iron - nickel films.** Shigeto Yamaguchi (Inst. of Phys. and Chem. Res., Tokyo). *Z. anal. Chem.*, 1960, **176** (1), 39–42.—Electron diffraction patterns show that the Fe:Ni ratio varies over the surface of an electrolytically deposited iron - nickel film. This inhomogeneity is confirmed by a previously described double-exposure technique (*cf.* Yamaguchi, *Anal. Abstr.*, 1959, **6**, 2986; Yamaguchi and Hori, *Ibid.*, 1960, **7**, 140) involving a magnetised sample; the displacement of the diffraction rings is proportional to the magnetic induction and thus varies with the Fe:Ni ratio. The film consists in fact of a mixture of discrete iron and nickel crystals. J. H. WATON

572. **Polarographic analysis of traces of metals in iron ores.** G. Odone and G. Picasso (Cornigliano S.p.A., Genoa, Italy). *Chim. e Ind.*, 1960, **42** (6), 598–605.—A series of rapid methods for the polarographic determination of Cu, Pb, Zn, Ni and Sn in iron ores has been developed. Procedures are reported for (*i*) Cu, Pb and Zn at pH 4 in M-KCl, (*ii*) Ni and Zn in M-NH_4Cl and M-aq. NH_3 and (*iii*) Sn in 6N-HCl, and some typical polarographic traces and results are given. By these procedures, traces of the metals named can be determined in iron ore in ≃ 2 hr. C. A. FINCH

573. **The determination of ferrous oxide in chromium ore and in chromium magnesite.** B. Brežný (Res. Inst. Metallurg. Ceram., Bratislava, Czechoslovakia). *Hutn. Listy*, 1960, **15** (7), 552–554.—The sample is dissolved in a mixture of H_3PO_4 and H_2SO_4 in the presence of an excess of $Ce(SO_4)_2$, the unchanged amount of which is titrated with a ferrous salt. *Procedure*—Mix the sample (0·2 g) with solid $Ce(SO_4)_2$ (0·2 g) and add a mixture of 85% H_3PO_4 and conc. H_2SO_4 (4:1). Heat at 280° to 300° till dissolution is complete. Dilute with H_2O and titrate potentiometrically with 0·05M-$(NH_4)_2SO_4.FeSO_4$. Carry out a blank. The determination requires 2 to 3 hr. J. ZÝKA

574. **Automatic gasometric titration of aqueous suspensions of ferrous hydroxide with oxygen.** B. Matseevskiĭ and L. Liepin'. *Izv. Akad. Nauk LatvSSR*, 1959, (12), 79–82; *Ref. Zhur., Khim.*, 1960, (14), Abstr. No. 56,721.—An automatic method is developed for the determination of Fe^{2+} by the absorption of O, and conditions are found for rapid quantitative absorption. The glass reaction vessel has a partition of about two-fifths of the internal diam. The $FeSO_4$ soln. is added to

the vessel down one wall of the partition, and NaOH soln. down the other. Oxygen is passed through the vessel in a thermostat, the vessel being connected to an automatic gas burette. The start of the reaction is taken as the initial time of shaking the reaction vessel; the O used is registered automatically. After completion of the reaction, completeness of the oxidation is checked by titrating the reaction mixture with dichromate in HCl medium. At 20° to 60° an aq. suspension of $Fe(OH)_2$ in the presence of excess of alkali is completely oxidised when vigorously shaken in an atmosphere of O, and O is quantitatively absorbed (relative error $\pm$ 1%). Ferrites are not formed as stable products. The procedure is recommended for use in analysis. C. D. KOPKIN

575. **Redoxokinetic titration of potassium ferricyanide against cobaltous sulphate.** K. Sundararajan (Central Electrochem. Res. Inst., Karaikudi, India). *J. Electroanal. Chem.*, 1960, **1** (4), 339–340 (in English).—To the ferricyanide soln. is added aq. NH_3 - ammonium citrate soln. and three platinum micro-electrodes are immersed in the soln. A stabilised c.d. of 0·5 mA per sq. cm is maintained between two electrodes, and the redoxokinetic potential (*cf.* Doss *et al.*, *Analyst*, 1958, **83**, 696) developed after each addition of cobaltous sulphate soln. is measured by using the third electrode. With 0·05M soln. a 150-μV peak is obtained, the derivative curve having a maximum value at one side of the peak. The precision as compared with potentiometric titration is $\pm$ 0·1%, falling to $\pm$1% with 0·01M soln.

R. M. S. HALL

576. **Preparation of spectrographic standards for magnesium in cast iron.** A. Argyle. *B.C.I.R.A. Journal*, 1960, **8** (4), 537–544.—Two-hundred samples of approx. percentage composition 3·5 C, 2·5 Si, 0·3 Mn, 0·05 P and $<$ 0·02 S obtained from large melts were examined with regard to composition, homogeneity, microstructure and grain size, as standards for use in the spectrographic determination of Mg in cast iron. A technique was devised which overcomes the difficulties of large-scale preparation of samples relatively consistent, sound and free from segregation.

C. H. COWPER-COLES

577. **Determination of graphitic carbon in cast iron.** F. Marion and R. Faivre (Fac. of Sci., Univ., Lille, France). *Chim. Anal.*, 1960, **42** (7), 355–359.—Values obtained in the determination of graphitic carbon in cast iron by the French standard method (AFNOR, No. A06-301) (digestion of sample with warm conc. HNO_3 and combustion of residue to yield CO_2) are liable to positive and negative errors, *viz.*, incomplete dissolution of Fe_3C and partial attack of the finer graphite particles. These two errors rarely compensate each other. A method of higher accuracy is based on the selective quant. conversion of the carbide C into hydrocarbons (mainly methane) by a gaseous mixture of steam and H (1:9) at 650° to 700° for a period from 30 min. to 4 hr. (determined initially for a specific type of cast iron), followed either by combustion of the unchanged graphite or oxidation of the hydrocarbons to CO_2 by passage over CuO at 900° to 950°. The sample should be ground to pass a 0·4-mm-mesh screen. Apparatus and procedure for each method are described. W. J. BAKER

578. **Determination of hydrogen in steel. Comparison of tin-fusion and hot-extraction techniques.** C. C. Carson (Materials and Processes Lab., Large Steam Turbine-Generator Dept., General Electric Co., Schenectady, N.Y.). *Anal. Chem.*, 1960, **32** (8), 936–939.—The same results are obtained by the tin-fusion technique at 1150° as by hot extraction at 975° or 650°. The standard deviations reported for these three procedures are, respectively, $\pm$0·14, $\pm$0·05 and $\pm$0·04 p.p.m. of H. The extra time involved in the hot-extraction method (30 min. as against 15 min.) is offset by gains in simplicity of apparatus and operational procedure.

T. R. ANDREW

579. **Polarographic determination of copper, zinc and chromium in cast-iron turnings.** J. Stabryn (Moravské Chem. Závody, Ostrava, Czechoslovakia). *Hutn. Listy*, 1960, **15** (4), 302.—*Procedure*—After dissolution of the sample (5 g) with HNO_3 and HCl, and removal of C and SiO_2 by the usual method, extract the Fe from the HCl soln. with ether, and dilute the acid soln. to 100 ml with H_2O. To an aliquot (20 ml) add conc. aq. NH_3 (5 ml), 5M-NH_4Cl (10 ml) and gelatin soln. (0·5%) (1 ml), dilute to 50 ml and register the polarographic waves of Cu (0 to $-$ 0·7 V) and Zn ($-$ 1·1 to $-$ 1·5 V). To a second aliquot (10 ml) add H_2O_2 (30%) (2 ml) and NaOH soln. (20%) (10 ml). Remove H_2O_2 by heating on a water bath, cool, add gelatin soln. (0·5%) (1 ml), dilute to 50 ml and register the polarographic wave of CrO_4^{2-} ($-$ 0·4 to $-$ 1·2 V). Evaluate the results by means of the method of standard addition. J. ZÝKA

580. **Direct photometric determination of aluminium in steel with Eriochrome cyanine R [C.I. Mordant Blue 3].** L. Doubek (Šmeralovy Závody, Brno, Czechoslovakia). *Hutn. Listy*, 1960, **15** (6), 477–478.—Of the methods tested, that of Hill (*Anal. Chem.*, 1959, **31**, 429) was the most suitable for various kinds of steel. J. ZÝKA

581. **Separation and determination of small quantities of aluminium in steel.** B. B. Bendigo and R. K. Bell (Nat. Bur. of Standards, Washington, D.C., U.S.A.). *J. Res. Nat. Bur. Stand., A*, 1960, **64** (3), 235–238.—The sample (5 g) is dissolved in a mixture of HCl and $HClO_4$, the soln. is evaporated to fuming (more HCl is added if $>$ 5% of Cr is present), then cooled, diluted with H_2O (200 ml), boiled and filtered. The filtrate (*A*) is reserved; the ignited ppt. is heated with H_2SO_4 - HF to remove SiO_2 and the cool acid-free residue is fused with $NaHSO_4$. The melt is extracted with H_2SO_4 (1:99); the soln. is boiled and filtered and the filtrate is added to *A* and the whole is made up to 500 ml with H_2O. An aliquot (100 ml) of this soln. is electrolysed in a mercury-cathode cell at 15 amp. for $\simeq$ 15 min. to remove most of the Fe. The electrolyte is then filtered, the filtrate is evaporated to $\simeq$ 50 ml and the pH is adjusted to 3·5 $\pm$ 0·1 with formic acid. The residual Fe, together with Al, Ti, V and other elements, is then extracted as cupferrate at 0° with $CHCl_3$ (three or four extractions are made). After removal of the $CHCl_3$ the cupferrates are converted into perchlorates and all the elements, except Al, are again extracted as cupferrates into $CHCl_3$. After removal of acids and unextracted cupferron from the aq. phase, the Al (0·02 to 0·3 mg) in an aliquot is determined spectrophotometrically at 540 mμ by the aluminon procedure of Pellowe and Hardy (*Analyst*, 1954, **79**, 225). The range covered is from 0·01 to 0·3%

of Al, and the accuracy is within ± 0·005%; two days are required for a complete determination.
W. J. BAKER

582. **Simultaneous determination of vanadium and titanium in steel.** R. J. Manuele and J. P. Sosa (Lab. de Ensayo de Mater. e Invest. Tecnológ., La Plata, Argentina). *Ind. y Quím.*, 1959, **19** (6), 433–434, 441.—*Procedure*—Dissolve the sample (1 g) in H_2SO_4 (1:10) (20 ml) and dilute the soln. to 100 ml with boiling water. Precipitate with 8% $NaHCO_3$ soln. (4 ml in excess), boil for 1 min. and filter. Wash the ppt. with hot water, dissolve it in a mixture of equal vol. of HNO_3 (1:1) and HCl (1:1), add conc. H_2SO_4 (5 ml) and evaporate twice to fuming. Dilute to 100 ml, mix an aliquot (25 ml) with water (50 ml) and remove residual Fe by electrolysis at 1 amp. for 1 to 1·5 hr., with a platinum-wire anode and a silver amalgam cathode (prep. described). Evaporate the soln. to 10 to 15 ml, add H_2SO_4 (1:1) (1 ml) and treat the mixture dropwise with 0·03N-$KMnO_4$ at 60° to 80° to a permanent pink colour. Cool, add 3% H_2O_2 soln. (2·5 ml) and dilute to 25 ml; transfer 12·5 ml to a colorimeter tube and read the extinction against a reagent blank with a No. 42 filter. Add KF (0·5 g) to the tube to bleach the colour due to Ti, and measure the residual extinction due to V. Refer results to a calibration curve. The method is simple, rapid, and sufficiently precise for classification purposes.
L. G. L. UNSTEAD-JOSS

583. **Line interference correction for X-ray spectrographic determination of vanadium, chromium and manganese in low-alloy steels.** P. D. Zemany (Res. Lab., Gen. Electric Co., Schenectady, N.Y., U.S.A.). *Spectrochim. Acta*, 1960, **16** (6), 736–741.—The low resolution of a LiF crystal was applied to the V - Cr - Mn system, in which V $K\beta$ interferes with Cr $K\alpha$, and Cr $K\beta$ interferes with Mn $K\alpha$, while V $K\alpha$ is the only 'free' line. The ratio of intensities found for $K\beta/K\alpha$ was, for V (with V_2O_5 as sample), 0·278, and for Cr (with $K_2Cr_2O_7$ as sample), 0·247. From these figures the contribution due to either of these elements in the sum of the intensities of a pair of interfering lines was calculated.
E. G. CUMMINS

584. **Spectrophotometric determination of small amounts of selenium in steel. II.** N. Léontovitch (Inst. Recherches de la Sidérurgie, Saint-Germain-en-Laye, France). *Chim. Anal.*, 1960, **42** (7), 329–335.—The method is based on the separation of Se from Fe, Mn, Ni, Cr, Mo, V, P and S in one operation, followed by the reduction of SeO_3^{2-} to Se by NaH_2PO_2 in the presence of As^{3+} as carrier and Cu^{2+} as catalyst. The colloidal Se is then determined spectrophotometrically as described in Part I (*Anal. Abstr.*, 1959, **6**, 4781). The sample (2 g) is dissolved in a cold mixture (1:2) of HCl and HNO_3, and the soln. (including that derived from the fusion of the insol. residue) is made up to 200 ml after the addition of a large excess of NaF to complex Si. An aliquot (20 ml is usual) is adjusted to be ≃ 6N in HCl and to contain 15N-formic acid (10 ml), As (10 mg, as $AsCl_3$), Cu (20 mg, as $CuSO_4$) and, if necessary, oxalic acid (10 g) (to complex Zr, Nb or Ta) and H_3PO_4 (20 ml) (to complex W). After removal of HNO_3 by heating and reduction with formic acid, the soln. is boiled (under reflux) for ≃ 40 min. with a mixture of conc. HCl and 40% aq. NaH_2PO_2. The ppt. is collected on a filter-disc (porosity 4), the co-pptd. As is dissolved in cold dil. HNO_3, and the red Se is then converted into grey Se by treatment of the ppt. with a few drops of 0·1% iodine soln. The Se is then dissolved in warm conc. HNO_3, the soln. is evaporated to ≃ 1 ml with the addition, during the final stages, of 15N-formic acid (5 ml) and 0·01% iodine soln. (2 or 3 drops). After ensuring the complete absence of iodine, HI and iodate, the soln. is made up to 20 or 50 ml for the spectrophotometric determination. Reproducibility and accuracy are high for contents of Se of ≃ 0·2 to 0·3%.
W. J. BAKER

585. **Determination of tungsten in high-alloy steels by isotope dilution.** G. Leliaert, J. Hoste and Z. Eeckhaut. *Rec. Trav. Chim. Pays-Bas*, 1960, **79** (6), 557–566 (in English).—An isotope dilution procedure with the use of ^{185}W for the determination of W in high-alloy steel is described. The W is determined spectrophotometrically with quinol in H_2SO_4 after homogeneous pptn. from a HNO_3 - H_2O_2 soln. No further chemical separations are required for Mo - V - W steels, but for steels containing Nb, Ta and/or Ti chemical separation of the elements that would interfere with the subsequent spectrophotometric determination is necessary. The magnesia extraction method of Powell *et al.* (*Analyst*, 1935, **60**, 509) can be successfully applied, as the Ti, Nb and Ta content can be reduced to < 0·3%, but since the recovery is rather low, W is determined photometrically and radiometrically in the filtrate. The method was successfully tested on a number of Nat. Bur. of Standards steels to which various amounts of Ta and Ti were added.
J. M. JACOBS

586. **Experiences with the use of secondary X-ray emission analysis for the determination of high contents of tungsten in steel.** O. Bělohlávek and J. Lažanský (SONP Kladno, Czechoslovakia). *Hutn. Listy*, 1960, **15** (7), 546–548.—The apparatus and method are described.
J. ZÝKA

587. **Indirect cerimetric determination of cobalt in steel.** F. Vydra and R. Přibil (Anal. Lab., Acad. Sci., Prague). *Hutn. Listy*, 1960, **15** (6), 476–477.—Cobaltous salts, in the presence of 1,10-phenanthroline (**I**), can be quantitatively oxidised with $FeCl_3$, and form an intensely red complex of Fe^{II} with **I**, namely ferroin, which can be titrated with $Ce(SO_4)_2$. *Procedure*—Dissolve the sample (0·5 to 1 g, containing 1 to 40% of Co) in aqua regia or other suitable mixture of acids and partly evaporate the soln. Cool and dilute the soln., filter off the undissolved $WO_3.H_2O$, wash it with HCl (1:10) and dilute the filtrate to 250 ml. Neutralise an aliquot with NaOH soln. till a turbidity appears, dissolve this in a few drops of HCl, and adjust the pH to 2 to 4. Add 0·1M-**I** (20 ml) (pH 3) and after 20 min. add 9N-H_2SO_4 (50 ml); dilute the mixture to 200 ml with H_2O and titrate potentiometrically with 0·05 to 0·1N-$Ce(SO_4)_2$. For samples with low contents of Co, a visual end-point can be used. The method is selective and accurate; Mn does not interfere.
J. ZÝKA

588. **Analysis of extracted residues [from alloy steels] by an X-ray fluorescence method.** H. Hughes and L. Gwilliam. *Metallurgia, Manchr*, 1960, **61** (367), 231–234.—Methods are described for the analysis of small amounts of residues extracted electrolytically from alloy steels, and include the determination of Fe, Co, Ni, Cr, V, Mo and Ti. Aluminium and Si are not considered, but it is thought that Cu, Zn and Mn could be determined.

Comparisons with conventional methods show good agreement of results. J. W. O. PYEMONT

589. **Quantitative determination of cobalt as tungstate.** V. D. Anand (Benares Hindu Univ., Vanarasi, India). *Ann. Chim., Roma*, 1960, **50** (3–4), 432–438.—A small excess of Na_2WO_4 soln. ($\simeq$ 0·5M) is added to the soln. containing 50 to 250 mg of Co (to give $\simeq$ 5 mg of W per mg of Co). Methanol is added to bring the concn. of alcohol to 50%; the pH is adjusted to 8·0 with N-HCl and the soln. is set aside for 1 hr. The ppt. of $CoWO_4.2H_2O$ is then filtered off, washed with aq. methanol, dried at 125° for 3 hr. and weighed. L. A. O'NEILL

590. **Conductimetric titration of cobalt as tungstate and selenite.** G. S. Deshmukh, V. D. Anand and A. K. Vishwanath (Benares Hindu Univ., Vanarasi, India). *Ann. Chim., Roma*, 1960, **50** (3–4), 439–444.—Cobalt may be determined conductimetrically by titration in 50% aq. ethanol with standard soln. of Na_2WO_4 or Na_2SeO_3. Under the conditions employed only the normal salts are formed. L. A. O'NEILL

591. **Differentiation of forms of cobalt in products of extractive metallurgy.** R. S. Young (2012 Paul's Terrace, Victoria, B.C., Canada). *Chemist Analyst*, 1960, **49** (2), 46.—Cobalt metal can be separated from a mixture with its oxides by passing Cl through a suspension of the sample in methanol. The metal dissolves rapidly whereas the oxides are attacked only slightly. If CoS is present, this also dissolves, but the time required is greater and then up to 3% of the Co_2O_3 and Co_3O_4 also dissolves. G. BURGER

592. **Separation of cobalt from its alloys and ores with 1-nitroso-2-naphthol.** E. Cogan (Albany Metall. Research Centre, Bureau of Mines, U.S. Dept. of the Interior, Albany, Ore.). *Anal. Chem.*, 1960, **32** (8), 973–975.—The sample soln. should contain 0·5 to 1·5 mg of Co, HCl (1:2) (10 ml) and ammonium citrate soln. (250 g of citric acid, 50 ml of H_2O and 250 ml of aq. NH_3) (20 ml) in 100 ml, at a pH of 3·5 to 4·0. Boil, add 1-nitroso-2-naphthol soln. (0·15% in 0·05N-NaOH) (25 ml), heat to incipient boiling, and set aside for 2 hr. in a cold-water bath. Extract with $CHCl_3$ (3 × 25 ml), combine the extracts and, after washing them with 5 ml of H_2O, evaporate to dryness. Fume the residue with H_2SO_4 (1 ml) and $HClO_4$ (1 ml) and finally heat to dryness. Take up the residue in H_2O and determine Co photometrically with nitroso-R salt. Iron, Ni, Cr, V, Mn, Zr and Ti do not interfere. Large amounts of Cu, Au and Pd interfere. T. R. ANDREW

593. **Photometric determination of trace amounts of cobalt in high-purity nickel.** C. L. Luke (Bell Telephone Lab., Inc., Murray Hill, N.J., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 836–837.—The sensitivity of the direct nitroso-R salt method for the photometric determination of Co (0·001 to 0·02%) in nickel can be increased without loss of accuracy by an initial separation of Co from a large sample (0·5 g) by converting it into a stable cobaltic ammine, followed by the pptn. of Ni as hexa-amminoperchlorate. Microgram amounts of Fe, Ti, Al and Mn must be complexed with citric acid, otherwise Co is co-pptd. on their hydroxides during the removal of Ni. By increasing the sample wt. and the light-path in the photometer, the lower limit of determination can be extended to 0·0001%. Provided that the bulk of the Fe is removed initially, the procedure is applicable to high-nickel steel. W. J. BAKER

594. **EDTA titration of cobalt in cemented carbides.** E. Lassner and R. Scharf (Metallwerk Plansee, A.-G., Reutte, Tirol, Austria). *Chemist Analyst*, 1960, **49** (2), 44.—The carbide sample is dissolved with HF and HNO_3. The soln. is diluted with water and, after the addition of tartaric acid, is made alkaline with aq. NH_3. The pH is adjusted to 4, an excess of EDTA soln. and a little ascorbic acid are added, the soln. is diluted with an equal vol. of methanol, and NH_4F and PAN indicator soln. are added. The excess of EDTA is titrated with 0·05 M-$CuSO_4$ at 70°. The results agree with those of a potentiometric method to within 0·5%. Nickel and V interfere. G. BURGER

595. **Spectrographic analysis of high-purity nickel.** R. L. Rupp, G. L. Klecak and G. H. Morrison (General Telephone and Electronics Laboratories Inc., Bayside, N.Y.). *Anal. Chem.*, 1960, **32** (8), 931–933.—A procedure is described that is suitable for the determination of Al, Co, Cr, Cu, Fe, Mg, Mn, Pb, Si, Sn, Ti and Zn in nickel at concn. of < 100 p.p.m. A Jarrell-Ash 3·7-metre grating spectrograph (15,000 lines per in. blazed for 3000 A) is used, with a 14-amp. d.c. arc, a 3-mm gap, a 15-μ slit width, a 10-sec. exposure, and Kodak 103-0 plates. The sample, in the form of powder, sheet or turnings, is tamped into a carbon cup-electrode and the exposure is made in an atmosphere of Ar (600 ml per min.) for Mg, Mn, Pb and Zn, or of N (600 ml per min.) for the other elements. Line intensities are read against Ni 2881·25 A, except for Cr, for which the unreported Ni line at 4244 A is used. A precision of $\pm$ 20% is reported. T. R. ANDREW

596. **Spectrophotometric determination of ruthenium with 1,4-diphenylthiosemicarbazide, with special reference to meteorites.** T. Hara and E. B. Sandell (Univ. Minnesota, Minneapolis, U.S.A.). *Anal. Chim. Acta*, 1960, **23** (1), 65–71.—Ruthenium (0·5 to 15 p.p.m.) is determined in iron and silicate meteorites with a recovery of $\simeq$ 95%. The initial treatment of the sample (1 to 2·5 g) yields a soln. in 10 ml of conc. H_2SO_4 and 40 ml of water. Solid $KMnO_4$ is added in slight deficiency, followed by 1% $KMnO_4$ soln. in slight (1 ml) excess and 1 g of sodium bismuthate. The soln. is distilled into 50 ml of a 0·1% soln. of $SnCl_2.2H_2O$ in 6N-HCl while air is bubbled slowly through it. Distillation is continued for 5 min. The distillate is treated with 3 ml of a satd. soln. of 1,4-diphenylthiosemicarbazide in methanol, heated in a boiling-water bath for 12 min., cooled, diluted to 100 ml with 6N-HCl and shaken for 1 min. with 5 ml of $CHCl_3$. The extinction of the extract is measured at 560 mμ and referred to a standard curve covering the range 0 to 20 μg of Ru. Osmium distils with the Ru, but does not interfere. H. N. S.

597. **Cation-exchange separation and spectrophotometric determination of microgram amounts of rhodium in uranium-base fissium alloys.** J. O. Karttunen and H. B. Evans (Argonne Nat. Lab., Lemont, Ill., U.S.A.). *Anal. Chem.*, 1960, **32** (8),

917–920.—After preliminary removal of U from HNO_3 soln. (1:1) by extraction with 30% tributyl phosphate in CCl_4, the HNO_3 soln. is evaporated to fumes with $HClO_4$ and the soln. is passed through a cation-exchange column (Dowex 50W-X8). Rhodium and Pd are retained on the column; Pd is eluted with 0·3M-HCl, and Rh is then eluted with 0·6M-HCl before photometric determination at 475 mμ after reduction with $SnCl_2$. The effect of various ions on the determination of Rh is reported.
T. R. ANDREW

598. **Polarographic determination of base-metal impurities in refined iridium.** N. K. Pshenitsyn, N. A. Ezerskaya and V. D. Ratnikova. *Anal. Blagorodnykh Metallov, Moscow, Akad. Nauk SSSR*, 1959, 70–74; *Ref. Zhur., Khim.*, 1960, (14), Abstr. No. 56,767.—The method is based on the chromatographic removal of Cu, Ni and Fe, with subsequent polarographic determination of Cu and Ni (in an ammoniacal basal soln.) and colorimetric determination of Fe as the sulphosalicylate complex. Dissolve the pressed plates of iridium in HCl (1:1) at 5 V and current density (a.c.) 0·15 amp. per sq. cm. Evaporate the resulting soln., containing about 5 g of Ir, to dryness, dissolve the residue in 500 ml of water, then add 0·5 g of NaCl and HCl to pH 1 and pass the soln. through a column (height 50 to 60 cm, diam. 2 cm) of cationite KU-2 at a rate of 4 to 5 ml per min.; wash the column with water and elute Cu, Ni and Fe with 150 to 200 ml of HCl (1:1) and the same vol. of water acidified with HCl. To the eluate add 0·5 g of NaCl, evaporate to dryness, add 0·5 ml of HCl and 50 ml of water, and pass the soln. through a small column of KU-2. Elute Cu, Ni and Fe with 100 ml of HCl (1:1), evaporate the eluate to small vol., add 1 or 2 ml of HNO_3 (to oxidise Fe^{2+}), boil, evaporate twice with HCl and make up to 25 ml. To determine Fe (with a content of Cu, Ni and Fe of $<$ 10 g per tonne, Fe is determined in a separate sample) add 5 to 10 ml of 10% sulphosalicylic acid soln. and aq. NH_3 in slight excess to 2 to 5 ml of the soln. and measure the extinction with a blue filter. To determine Cu and Ni, evaporate an aliquot of the soln. to 1 or 2 ml, make up to 10 ml with the basal soln. (N-NH_4Cl and aq. NH_3), add 0·1 g of Na_2SO_3 and 2 or 3 drops of 0·05% gelatin soln. and record the polarogram. Carry out controls concurrently. The method gives satisfactory results with contents of Cu of 4 to 400 g, Ni 2 to 400 g, and Fe 10 to 600 g per tonne of refined iridium.
C. D. KOPKIN

599. **Polarographic determination of platinum on the rotating platinum micro-disc electrode.** V. S. Temyanko, M. B. Bardin and Yu. S. Lyalikov. *Izv. Vyssh. Uchebn. Zavedenii, Khim. i Khim. Tekhnol.*, 1959, **2** (4), 503–508; *Ref. Zhur., Khim.*, 1960, (8), Abstr. No. 30,499.—The polarographic behaviour of H_2PtCl_6 is studied on a rotating platinum disc electrode (a platinum wire of diam. 1 mm fused into a glass tube of diam. 5 to 6 mm and polished; surface area of the disc 0·78 sq. mm). In a basal soln. of 0·1M-$NaNO_3$, H_2PtCl_6 gives two waves, the first of $E_{\frac{1}{2}} = -0{\cdot}343$ V (*vs.* the S.C.E.) corresponding to the irreversible reduction of Pt^{IV} to metal with transfer of 4 electrons (calculated from the Ilkovic equation) and the second corresponding to reduction of H^+. Increasing the $NaNO_3$ concn. causes a slight increase in the height of the wave due to Pt; changing the HNO_3 concn. from 10^{-5} to 2M does not affect the height of the platinum wave, but increases the hydrogen wave. In the presence of NaCl ($> 10^{-4}$M), NaBr or NaI, the platinum wave decreases and disappears, while the hydrogen wave is retained and is only slightly displaced towards the region of positive potentials. It is recommended to use a basal soln. of 0·1N-$NaNO_3$ for the polarography of Pt. The electrode is first cleaned with emery cloth, wiped with damp filter-paper, and platinised for 5 or 6 min. at 1·0 V, or 2 or 3 polarograms of Pt are recorded at a potential below the hydrogen reduction potential. A platinum plate of area 400 sq. mm is used as anode. Nitrogen is passed for 30 to 40 min. through the basal soln. (20 to 25 ml of 0·1M-$NaNO_3$), the soln. of Pt^{IV} is added, N is passed for a further 3 to 4 min., and the polarogram is recorded. The height of the platinum wave is proportional to the concn. of Pt in the range $3{\cdot}6 \times 10^{-5}$ to $7{\cdot}2 \times 10^{-4}$M. The error is $\pm$ 5%.
C. D. KOPKIN

600. **Micro-heterometric determination of platinum, palladium and gold with papaverine.** M. Bobtelsky and M. M. Cohen (Hebrew Univ., Jerusalem, Israel). *Anal. Chim. Acta*, 1960, **23** (1), 42–56.—The heterometric method is applied to the titration of Pt^{4+}, Pd^{2+} and Au^{3+} (0·3 to 0·5 mg), singly and in the presence of each other, with 0·00075 to 0·004M-aq. papaverine. The titrations are performed in the presence of halide ions or SCN^-.
H. N. S.

601. **Microchemistry of the platinum metals. Separation and determination of micro amounts of ruthenium, rhodium and palladium.** F. Jasim, R. T. Magee and C. L. Wilson. *Rec. Trav. Chim. Pays-Bas*, 1960, **79** (6), 541–550 (in English).—The method is based on the reactions of the metals with 8-hydroxyquinoline. Determinations are carried out spectrophotometrically on the $CHCl_3$ extract of the metal 8-hydroxyquinolinate. For the separation of the metals, the soln. is treated with 1% aq. methyltriphenylarsonium iodide and 3N-NaCl and the Pd is extracted with $CHCl_3$. The Ru is then separated from the Rh by treatment with the 8-hydroxyquinoline - $CHCl_3$ reagent in the presence of sufficient 10% Na acetate soln. to make the pH $\simeq$ 6·4, when the Ru is extracted in the $CHCl_3$ layer. The procedure gives reproducible results and provides a rapid method for the determination of these metals.
J. M. JACOBS

602. **Chemical composition of chromites.** S. A. Bilgrami and C. O. Ingamells (Dept. of Geol., Univ. Minnesota, Minneapolis). *Amer. Miner.*, 1960, **45** (5–6), 576–590.—Full details are given for the complete analysis of chromite ore samples. Silicon, Al, Ti, total Fe, Ca, Mg and H_2O are determined by the usual techniques, particular care being taken to determine Cr in the ammonia group ppt., though the major part of the Cr is determined in the filtrate. For Fe^{II} an indirect method is described, based on the original procedure of Seil (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 189). Manganese is determined colorimetrically and V is pptd. with cupferron and determined colorimetrically as peroxovanadate.
R. A. HOWIE

See also Abstracts—**417**, Thionol as reagent for Sn^{II}, Cr^{II} and Ti^{III}. **418**, New Nessler reagent for NH_3. **659**, Na_2S in presence of thiols. **660**, **696**, H_2S in presence of thiols. **794**, Bi in pharmaceutical products. **809**, Thallium in wine. **879**, Oxygen in gases.

3—ORGANIC ANALYSIS

Determination of elements and radicals and of organic compounds not included in other sections. Organic industrial products, including petroleum and its products, fuels, detergents, volatile oils, cosmetics, dyestuffs, fibres, plastics, resins, paints, elastomers, leather, explosives, etc.

603. **Determination of active hydrogen using exchange with deuterium. Infra-red spectrophotometric method.** W. R. Harp, jun., and R. C. Eiffert (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 794–796.—In the general method described, the sample is mixed with a relatively large amount of ^2H_2O and the amount of active hydrogen is calculated by the method of Gaunt (*Analyst*, 1954, **79**, 580) from the intensity of the 2·97-μ OH band in the ^2H_2O phase. Samples sol. or insol. in water can be analysed in $\simeq$ 30 min. with an accuracy of $\simeq$ 2% of the amount of active hydrogen present. K. A. PROCTOR

604. **Conductimetric micro-method for determining carbon in organic compounds.** S. Greenfield [Albright & Wilson (Mfg.) Ltd., Res. Dept., Oldbury, Birmingham, England]. *Analyst*, 1960, **85**, 486–492.—In the method described, the conventional absorption tube in Pregl's combustion train is replaced by a conductimetric cell containing KOH soln. The cell and the procedure for its calibration and for the determination of C in 1-mg amounts of organic compounds are described. The method is more accurate than the conventional Pregl method when similar weights of sample are used. The reproducibility is $\pm$ 0·29 μg of C in 1-mg samples. A. O. JONES

605. **Apparatus for the flask combustion of organic compounds adaptable to carbon determination.** F. W. Cheng and C. F. Smullin (Chem. Res. Dept., Atlas Powder Co., Wilmington, Del., U.S.A.). *Microchem. J.*, 1960, **4** (2), 213–215.—A modified Schöniger flask is described and illustrated. The sample in a porcelain boat is ignited by contact with heated platinum gauze; the CO_2 evolved is pptd. as $BaCO_3$, which is then dissolved in acid and the excess of acid is back-titrated. The apparatus is also suitable for the determination of H. P. D. PARR-RICHARD

606. **Oxidation processes in elementary analysis. III. Activation and de-activation of oxidation layers used in carbon dioxide atmospheres.** G. Kainz and H. Horwatitsch (Anal. Inst., Univ., Wien). *Z. anal. Chem.*, 1960, **176** (1), 17–27 (in German).—The surface layer of a copper oxide catalyst suffers deactivation, on heating in CO_2, by the loss of O to form Cu_2O, but is activated by re-oxidation on heating in O. The effect of deactivation is less marked at higher combustion temp., owing to the higher velocity of the reaction between the sample and O. J. H. WATON

607. **Oxidation processes in elementary analysis. II. Preparation of highly reactive packings for tubes in the determination of nitrogen.** G. Kainz and H. Horwatitsch (Anal. Inst., Univ., Wien, Austria). *Z. anal. Chem.*, 1960, **175** (4), 272–280 (in German).—The efficacy of CuO is greatly increased by an increase in the effective surface area (achieved by the use of pptd. CuO of particle size $< 1\mu$) and by impregnation with silver, cobalt oxide or Cr_2O_3. The time for an analysis is thus greatly reduced and lower temp. can be used. A layer 5 cm long maintained at 550° suffices for the determination of traces of N in mineral oil. J. P. STERN

608. **Oxidation processes in elementary analysis. I. The efficiency of the oxidative layer in the Pregl determination of carbon, hydrogen and nitrogen.** G. Kainz and H. Horwatitsch (Anal. Inst., Univ., Wien, Austria). *Z. anal. Chem.*, 1960, **175** (3), 166–174 (in German).—As confirmed with methane, a combustion temp. of 680° suffices for the quant. oxidation of any cracking products in elementary analysis when the standard gas velocity is maintained. At higher velocities in the combustion zone, caused by pyrolytic gas evolution, the proportion of unburnt methane increases noticeably and higher temp. are necessary. This applies particularly to automatic combustion trains, for which furnace temp. of 780° and 830° are recommended for C and H, and for N determinations, respectively. J. P. STERN

609. **Micro-determination of nitrogen by Dumas method.** T. S. Gore and A. S. Kulkarni (Dept. of Chem. Technol., Univ., Bombay, India). *Mikrochim. Acta*, 1960, (4), 559–566 (in English).—Pure CuO (99·6%) is unsatisfactory at 730° as a Pregl filling for Dumas micro-determinations. It is modified by the introduction of a second roll of reduced copper gauze just within the end of the hot zone; this filling gives results of high accuracy. Calibration methods are detailed. J. P. STERN

610. **Dumas micro-determination of nitrogen; calibration of nitrometer.** E. Stehr (Res. Centre, Texaco Inc., Beacon, New York, U.S.A.). *Microchem. J.*, 1960, **4** (2), 207–212.—The Dumas or Pregl micro-nitrometer is readily calibrated by introducing accurately measured increments of N from a micro-burette into the graduated portion. The vol. of N equiv. to each scale division is determined and corrected for temp. and pressure by use of a general equation. P. D. PARR-RICHARD

611. **Direct volumetric determination of ammonia in the Kjeldahl process.** E. Schulek, K. Burger and M. Fehér (L. Eötvös Sci. Univ., Budapest). *Magyar Kém. Foly.*, 1960, **66** (7), 250–251.—This is a version (in Hungarian) of the paper published (in German) in *Z. anal. Chem.*, 1959, **167**, 28; *cf. Anal. Abstr.*, 1960, **7**, 168.

612. **Micro-determination of halogens in organic compounds. I. New method for the micro-determination of chlorine in organic compounds containing carbon and chlorine; carbon, hydrogen and chlorine; and carbon, hydrogen, oxygen and chlorine.** A. A. Abramyan and R. S. Sarkisyan. *Izv. Akad. Nauk ArmSSR, Khim. Nauka*, 1959, **12** (5), 341–344; *Ref. Zhur., Khim.*, 1960, (9), Abstr. No. 34,568.—The samples are decomposed in sealed refractory glass tubes of length 18 to 20 cm and internal diam. 8 to 10 mm. For solids and non-volatile liquids, 100 to 150 mg of powered $KMnO_4$ is added to the sample (7 to 16 mg) in the ignition tube; for volatile liquids the $KMnO_4$ is first placed in the tube, followed by the sample in an open ampoule. The sealed tube is heated at 300° to 500° for 1 hr. (the temp. and time of heating depending on the substance), the contents of the tube are washed out with 30 to 40 ml of water, 1 to 1·5 ml of 0·5N-HNO_3 is added, the soln. is heated to boiling to destroy traces of $KMnO_4$, and 5 to 10

drops of 6% H_2O_2 soln. are added. After cooling, the soln. is titrated with 0·025N-$Hg(NO_3)_2$ in the presence of diphenylcarbazone. The error is 0·5%.
C. D. KOPKIN

613. **Rapid micro-methods of elemental analysis. I. Determination of chlorine in organic compounds.** E. C. Olson and A. F. Krivis (The Upjohn Co., Kalamazoo, Mich., U.S.A.). *Microchem. J.*, 1960, **4** (2), 181–186.—Methods for the determination of Cl after combustion by the Schöniger technique are critically discussed; coulometric titration with electrically generated Ag^+, with potentiometric detection of the end-point with a calomel reference electrode and a silver indicating electrode, was satisfactory. After burning the sample in O and absorbing the products in 0·2M-NaOH, the soln. is acidified with HNO_3 and titrated to a set potential (previously determined on a reference material). The standard deviation for 12 determinations on a sample containing 22·45% of Cl was ± 0·09.
P. D. PARR-RICHARD

614. **Qualitative detection of iodine in organic compounds.** J. G. Sharefkin and H. E. Schwerz (Dept. of Chem., Brooklyn College, N.Y., U.S.A.). *Anal. Chem.*, 1960, **32** (8), 996–998.—The procedure described, which can be used to distinguish iodine from bromine and chlorine, is based on the formation of an acetate ester with 40% peroxyacetic acid. After reaction with hydroxylamine, the ester is detected as a wine-red ferric ligand with acetohydroxamic acid.
K. A. PROCTOR

615. **Micro-determination of boron in organic boron compounds.** S. K. Yasuda and R. N. Rogers (Univ. of California, Los Alamos Sci. Lab., N. Mex.). *Microchem. J.*, 1960, **4** (2), 155–161.—The sample (≡0·5 to 1 mg of B), together with 10 mg of sucrose, is burned in O by the Schöniger technique and the products are absorbed in 10 ml of H_2O. The soln. is transferred with 5 ml of methanol to the cathode compartment of a coulometric titration cell, 1 ml of satd. $NaNO_3$ soln. is added to both cathode and anode compartments, and the liquid level in the latter is adjusted with H_2O. Any strong acid is pre-titrated to pH 7, 1·6 to 1·7 g of mannitol is added, and the H_3BO_3 is titrated to the potentiometric end-point. The curve of pH *vs.* time interval is plotted, and the end-point is established by the method of concentric arcs (Tubbs, *Anal. Abstr.*, 1955, **2**, 267). If Cl is present, a little 30% H_2O_2 soln. is added to the flask before combustion. Recoveries of B are good except with very refractory materials such as boron carbide.
P. D. PARR-RICHARD

616. **Determination of selenium in organic substances.** E. Meier and N. Shaltiel (Microanal. Lab., Weizmann Inst., Rehovoth, Israel). *Mikrochim. Acta*, 1960, (4), 580–583 (in German).—The iodimetric determination of SeO_2 obtained by combustion of the organic sample permits the determination of 1 to 2 mg of Se with an accuracy within ± 2%. *Procedure*—Burn the sample (3 mg) in O either in a quartz tube at ≃300° or in a Schöniger flask, flush the SeO_2 into H_2O, add KI (50 mg) and 2N-H_2SO_4 (10 ml) and titrate the pptd. iodine after 5 min. with 0·01N-$Na_2S_2O_3$.
J. P. STERN

617. **Determination of the sulphonyl chloride group in *m*-benzenedisulphonyl chloride.** J. E. Barker, C. M. Payne and J. Maulding (Tennessee Corp., College Park, Ga., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 831–832.—The method is based on the hydrolysis of the sulphonyl chloride group in the presence of pyridine and the subsequent titration of the liberated sulphonic and hydrochloric acids with NaOH soln., phenolphthalein being used as indicator. The results agreed to within ± 0·1% with those obtained by the method of Neitzel (*ChemikerZtg*, 1919, **43**, 500) and were consistent with the purity of the compound as determined by elementary analysis.
G. P. COOK

618. **Conductimetric titration of very weak bases in aqueous medium.** F. Gaslini and L. Z. Nahum (Res. Div., Cartiera Vita Mayer & Co., Milan, Italy). *Anal. Chem.*, 1960, **32** (8), 1027–1029.—Twenty-five weak bases with ionisation constants between 10^{-5} and 10^{-12} were titrated conductimetrically. The determinations were carried out by dissolving the samples in an excess of aq. acetic acid and titrating with 2N-trichloroacetic acid. The titration curves had sharp angles at the end-points, and recoveries ranged from 96·3% to 101·8%. The method was also applied to the differential titration of di-acid bases and mixtures of mono-acid bases.
G. P. COOK

619. **Gas chromatography of C_1 to C_4 hydrocarbons on organophilic silica.** C. Rossi, S. Munari, L. Cengarle and G. F. Tealdo (Ist. Chim. Ind., Univ. Genoa). *Chim. e Ind.*, 1960, **42** (7), 724–727.—Silica powders partially covered with organic radicals, obtained by esterification with alcohols, are used for gas-chromatographic columns for the analysis of C_1 to C_4 hydrocarbon mixtures. The best results are obtained with silica powder esterified with benzyl alcohol; good results are also obtained with lauryl alcohol, with 2 to 4-metre columns at room temp. Various chromatograms obtained with these systems are illustrated, showing useful separations of mixtures containing, *e.g.*, but-1-ene, but-2-ene, n-butane, isobutane, butadiene, propene and propane. These stable adsorbents may, by changing the organic radicals, be used for other analytical procedures.
C. A. FINCH

620. **Two highly selective solvents for gas - liquid chromatography analysis of C_2 to C_6 hydrocarbons.** A. van der Wiel (Koninklijke/Shell Lab., Amsterdam). *Nature*, 1960, **187**, 142–143.—Two liquids, dimethyl sulphoxide (**I**) and sulpholane (tetramethylene sulphone) (**II**), are suggested for the analysis of complex C_2 to C_6 hydrocarbon mixtures. The column is packed with C-22 firebrick, 50 to 80 mesh (length 14·4 metres for **I**, 18·0 metres for **II**, and internal diam. 6 mm), and the wt. ratio of solvent to solid support is 3:7. The H flow rate is 5 litres per hr. for **I** and 4 litres per hr. for **II**, while the column temp. is kept at 30° ± 0·1°. The separation efficiency is high and compounds with closely similar b.p., but different molecular types, can easily be separated. **I** and **II** do not react with unsatd. compounds but, with acetylenic compounds containing active H atoms, glass or stainless-steel tubing is required, since they react with copper tubing in the presence of **I**. The time of analysis is short (about 30 min. for complex mixtures), and the sample required is small.
R. A. HENDEY

621. **Gas - solid chromatographic separation of hydrocarbons of high molecular weight.** C. G. Scott and D. A. Rowell (Lobitos Oilfields Ltd., Ellesmere Port, Ches., England). *Nature*, 1960, **187**, 143–144.—A method is described whereby alumina, deactivated with inorganic bases and salts in aq.

soln., is used as a column packing for separation of high-mol.-wt. hydrocarbons. Results are given for C_{18} to C_{28} (column temp. 250°) and C_{20} to C_{36} (column temp. 320° to 390°) n-paraffins. By reduction of the activity of the modified alumina and the use of a high-sensitivity detector and a high temp., separation of n-paraffins higher than C_{50} should be possible. R. A. HENDEY

622. **Continuous trace-hydrocarbon analysis by flame ionisation.** A. J. Andreatch and R. Feinland (Central Res. Div., American Cyanamid Co., Stamford, Conn., U.S.A.). *Anal. Chem.*, 1960, **32** (8), 1021–1024.—An inexpensive, rugged and portable flame ionisation detector designed for the continuous analysis of trace amounts of hydrocarbons is described. It is insensitive to inorganic gases, but responds to hydrocarbons in proportion to the carbon atom content. The limit of detection of hexane is 1 in 10^9. In combination with a chromatographic column the detector can be used to separate and determine methane, ethane, ethylene, acetylene and propene. K. A. PROCTOR

623. **Application of diffusion cells to the production of known concentrations of gaseous hydrocarbons.** A. P. Altshuller and I. R. Cohen (R. A. Taft San. Engng Center, U.S. Dept. Health, Educ. and Welfare, Cincinnati, Ohio). *Anal. Chem.*, 1960, **32** (7), 802–810.—The process essentially involves the diffusion of molecules evaporated from a liquid reservoir into a space containing a diluent gas flow. Diffusion coefficients were determined for a number of hydrocarbons at various temp. and the effect of turbulence at the end of the diffusion tube, resulting from the rapid flow of carrier gas over the top of the tube, was investigated as a function of gas-flow rate, temp., diffusion-tube diam., and tube length. The results should aid in defining the experimental limits within which a diffusion apparatus may be operated. G. P. COOK

624. **Spectrophotometric determination of olefins in concentrated sulphuric acid.** A. P. Altshuller, S. F. Sleva and A. F. Wartburg (U.S. Dept. Health, Educ. and Welfare, Cincinnati, Ohio, U.S.A.). *Anal. Chem.*, 1960, **32** (8), 946–954.—The method is based on the absorbance produced in the 300 to 310-mμ range by the reaction of olefins with conc. H_2SO_4. The procedure is insensitive to ethylene, and to propene concn. below 1500 p.p.m. Propyl and higher-mol.-wt. alcohols, some high-mol.-wt. aldehydes, NO_2 and SO_2 interfere. The method was applied to some two-component liquid mixtures and to gas mixtures containing butenes, hex-1-ene or hex-1-ene - benzene in air. The suitable concn. range is 100 to 10,000 p.p.m. G. P. COOK

625. **Qualitative detection of olefins by ozonolysis.** J. G. Sharefkin and A. Ribner (Brooklyn Coll., New York, U.S.A.). *J. Chem. Educ.*, 1960, **37** (6), 296–297.—The test is based on the Harries reaction, in which ozone is added to the C to C double bond, forming an ozonide, which is then reductively hydrolysed to produce two carbonyl groups. For the detection of the carbonyl compound, a modification of the Bonner procedure (*Ibid.*, 1953, **30**, 452) is used. *Procedure*—The olefin (0·1 g) is dissolved in a soln. of 2,4-dinitrophenylhydrazine (0·05M in methanol with HCl added to a concn. of 2N). Ozonised air is passed through the soln. for up to 4 min., then a drop of the reaction mixture is pipetted into KOH soln. (2 ml of 2M in methanol). A deep-red coloration indicates a positive test. Peroxides formed between some alkenes and O in the ozonised air also give a positive test. A cheap ozoniser is described which should enable the test to be carried out in laboratories not equipped with a commercial apparatus. G. S. ROBERTS

626. **Detection and characterisation of olefins as 2,4-dinitrophenylhydrazones of methyl ketones formed by the Friedel - Crafts acetylation.** J. G. Sharefkin and T. Sulzberg (Brooklyn Coll., N.Y., U.S.A.). *Anal. Chem.*, 1960, **32** (8), 993–996.—A wine-red colour is produced when a base is added to the 2,4-dinitrophenylhydrazone. The reaction has been used to characterise olefins and to determine the degree of olefinic character in unsaturated hydrocarbons. G. P. COOK

627. **Determination of trace water in butane by gas chromatography.** A. A. Carlstrom, C. F. Spencer and J. F. Johnson (California Res. Corp., Richmond, U.S.A.). *Anal. Chem.*, 1960, **30** (8), 1056.—The method described has a limit of detectability of 0·2 p.p.m. of water in a 10-litre sample of butane. The water in the sample is concentrated in a trapping device consisting of 1 ft. of one-quarter-inch copper tubing packed with 30% polyoxyethylene glycol on 20 to 30-mesh firebrick, maintained at 10°. After the water has been trapped from a measured vol. of sample, the trap is heated to 90° and the water vapour is flushed into the gas chromatograph with a stream of He. The analysis is carried out on a 2-ft. column packed with the same material as the trap, and operating at 80° with a He flow of 100 ml per min. Under these conditions the retention time for water is 11·5 min. At the 160-p.p.m. level of water, the standard deviation (5 assays) was 24 p.p.m. and at the 15-p.p.m. level (5 assays) it was 2·7 p.p.m. K. A. PROCTOR

628. **Technique for handling volatile liquid samples; index of refraction of system n-heptane - benzene.** J. E. Powers (School of Chem. Engng, Univ. of Oklahoma, Norman, U.S.A.). *Chemist Analyst*, 1960, **49** (2), 54.—Values of refractive index at 25° are presented for 18 mixtures of n-hexane (pure grade, 99%) and benzene (reagent grade). G. BURGER

629. **Fluorine chemistry. IV. Gas - liquid chromatography of fluorocarbons.** H. Rotzsche (Inst. f. Silikon- und Fluorkarbon-Chem. Radebeul-Dresden, Germany). *Z. anal. Chem.*, 1960, **175** (5), 338–350.—The observation of interchange effects between fluoro-, chlorofluoro- and bromofluorohydrocarbons and the polar stationary liquid phase has led to the development of the gas-chromatographic method described, which by a graphical presentation technique permits the detection of homologous series and the calculation of selectivity coefficients. E. G. CUMMINS

630. **Purity test on carbon tetrachloride and benzene with the UR 10 infra-red spectrophotometer.** K. Palm (Friedrich-Schiller Univ., Jena). *Chem. Tech., Berlin*, 1960, **12** (7), 402–406.—The use of the instrument, fitted with a lithium fluoride prism, is studied. Data given include—characteristics of impurities in CCl_4 (CS_2, cyclohexane, $CHCl_3$, trichloroethylene and H_2O), and in benzene (thiophen, toluene, xylene, CS_2, cyclohexane and methylcyclohexane), and absorption spectra of the fractions obtained in the distillation of CCl_4. It is concluded that the spectrophotometer gives accurate results, though the method is simpler for CCl_4 than for benzene. E. M. MAYES

631. **Colorimetric determination of low concentrations of primary and secondary alcohols.** D. P. Johnson and F. E. Critchfield (Union Carbide Chem. Co., South Charleston, W. Va., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 865–867.—The method is based on the reaction of the alcohols with 3,5-dinitrobenzoyl chloride in pyridine and the subsequent treatment of the esters with a soln. of dimethylformamide and propylenediamine to produce a red quinonoidal ion. The colour is measured at 525 mμ. Concn. of 2 to 100 μg can be determined in the presence of acetals, vinyl ethers and other acid-hydrolysable compounds with an accuracy of ± 2%. G. P. Cook

632. **Colorimetric determination of secondary alcohols by conversion to ketones.** F. E. Critchfield and J. A. Hutchinson (Union Carbide Chem. Co., South Charleston, W. Va., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 862–865.—The sample is oxidised with $K_2Cr_2O_7$ in acid soln. (H_2SO_4) and the ketone formed is determined colorimetrically with 2,4-dinitrophenylhydrazine. Primary alcohols are oxidised to acids and do not interfere. Reaction rates are listed for the determination of 10 secondary alcohols; a separate calibration curve is required for each. The method is also applicable to the determination of ketones in the presence of aldehydes. G. P. Cook

633. **Spectrophotometric determination of butyl alcohols.** Ya. E. Shmulyakovskii. *Khim. i Tekhnol. Topliv i Masel*, 1959, (12), 46–50; *Ref. Zhur., Khim.*, 1960, (14), Abstr. No. 56,786.—The u.v. absorption spectra of the isomeric butyl nitrites are studied. The nitrites from normal (**I**), secondary (**II**) and isobutyl alcohols differ in their extinction values, but the absorption bands of the nitrite from tertiary butyl alcohol (**III**) have different positions and intensities. To analyse a mixture of butyl alcohols, shake 10 ml of heptane with 10 ml of an aq. soln. of the sample (a few mg of alcohols), 0·5 ml of 0·5N-HCl and 0·5 ml of 2·5% $NaNO_2$ soln., and discard the aq. layer. Add 10 ml of 0·5N-ammonium carbonate, shake, and again discard the aq. layer. Measure the extinction of the resulting soln. of the butyl nitrites in heptane. The method can be used to determine **II** in the products of its oxidation to ethyl methyl ketone; the measurements are made at 347, 358 and 372 mμ; the error is ≯ 1%. To determine **II** and **III**, measure at 353, 358, 367, 372, 382 and 399 mμ; for **I** and **II**, at 357 and 376 mμ; and for **I**, **II** and **III**, at 357, 372 and 399 mμ; formulae are given for calculating the contents of the components in these mixtures. The total content of butyl alcohols is determined by the absorption at 385 mμ.
C. D. Kopkin

634. **Chromatographic determination of ether in condensates from the Lebedĕv synthesis of butadiene.** M. Kubínová (Res. Inst. Synth. Rubber, Gottwaldov, Czechoslovakia). *Chem. Průmysl*, 1960, **10** (7), 359–360.—A gas-chromatographic method for the separation of butadiene, acetaldehyde, ethyl ether and ethanol is described. The procedure was carried out on a 3-metre column filled with a mixture of kieselguhr (24 g) and dioctyl phthalate (8 g), with H as the carrier gas at 70°. The results were in good agreement with those obtained with artificially prepared mixtures and with the hydroxylamine method for the determination of acetaldehyde. J. Zýka

635. **Determination of trimethylene glycol [propane-1,3-diol] in glycerol by gas chromatography.** J. Clifford (Unilever Ltd., Port Sunlight, Ches., England). *Analyst*, 1960, **85**, 475–478.—The column is a mixture of Reoplex 400 and Celite (1:3) previously heated in N at 200° to remove volatile matter. The sample is diluted with twice its vol. of ethanol, a portion (≡≃ 0·04 μl of glycerol) is transferred to the column, and the chromatogram is recorded under specified conditions. The areas under the propane-1,3-diol and glycerol peaks are measured, the amount of propane-1,3-diol present is calculated as a percentage of the total propane-1,3-diol and glycerol content of the mixture, and the result is corrected by means of a calibration graph prepared with known mixtures of the two compounds. The method is applicable to mixtures containing as little as 0·1% of propane-1,3-diol, and, with the apparatus used (a Pye argon chromatograph), the accuracy is within ± 10%. Impurities usually present in crude glycerol do not interfere.
A. O. Jones

636. **Separation of carbohydrates on anion-exchange resins.** L. Hough, J. E. Priddle and R. S. Theobald (Dept. of Chem., Univ., Bristol, England). *Chem. & Ind.*, 1960, (28), 900.—Raffinose, sucrose and D-glucose are separated by elution with water from a column of De-Acidite SRA 68 (3·5% cross-linked) in chloride, carbonate or bicarbonate form, in the order of decreasing mol. size. L-Arabinose could be separated from D-xylose, D-ribose and D-lyxose, which are themselves inseparable in this way. No separation occurs with 8% cross-linked polystyrene beads, so that separation is not caused by a mol. sieve effect. Electrophoresis in carbonate soln. gave no useful results. E. J. H. Birch

637. **The chromatography of starches. I. Paper chromatography.** Motoji Taki (Fac. of Agric., Univ., Tsu, Mie, Japan). *J. Agric. Chem. Soc. Japan*, 1959, **33** (3), 216–218.—Paper chromatography of starches is carried out by the use of paper that has been washed successively with 15% KOH soln. and water, then dried; N-KOH is used as the developing solvent, with the descending technique. After development the strip is immediately immersed in 10% acetic acid soln. and the spots are revealed by ethanolic iodine soln. The amylose fraction moves to the middle of the strip, and the amylopectin fraction remains at the origin.

II. Quantitative paper chromatography. Motoji Taki. *Ibid.*, 1959, **33** (3), 218–220.—The method was modified for quantitative determination. A sample of starch soln. (10 mg per 10 ml of 0·5N-KOH) (0·05 ml) is placed at the origin of the strip and developed with 0·8N-KOH. The amylose fraction, which migrates to the bottom end of the strip, is collected and determined colorimetrically with iodine after neutralisation with acetic acid. Potato and rice amylose can be determined by this method.

III. Separation and determination of amylose in starches. Motoji Taki. *Ibid.*, 1959, **33** (4), 245–249.—Starch soln. is spotted on a paper that has been treated with 15% KOH soln. and 35% $HClO_4$, and developed with 35% $HClO_4$ soln. by the descending technique. The amylopectin fraction remains at the origin, while the amylose fraction, contaminated with a slight amount of amylopectin, descends with the solvent front. The amylopectin band is cut off and the remaining strip is developed once again by $HClO_4$ soln. after exposure to iodine vapour. The blue amylose fraction remains

stationary, but a reddish-violet band of impure amylopectin is eluted. After washing the strip with ethanolic iodine and drying in air till the colour is discharged, the amylose fraction is eluted with 35% $HClO_4$ soln. and determined colorimetrically.

IV. Determination of the amylose contents of various starches by paper chromatography. Motoji Taki. *Ibid.*, 1959, **33** (6), 445–448.—The paper-chromatographic determination of amylose in starch, with $HClO_4$ as developer, was further examined and the results were compared with those obtained by the use of standard amylose soln. Amylose in 10 kinds of starch was determined by this method, and the results were compared with those obtained by existing methods.

V. New method for the paper chromatography of starches. Motoji Taki. *Ibid.*, 1959, **33** (6), 448–452.—The same procedure was carried out in an iodine atmosphere. After the elution of the amylopectin fraction, the amylose fraction was collected with a satisfactory purity and recovery. By this method the contaminant in the amylopectin fraction, separated by the butanol method from starch, was separated to reveal amylose of a lower degree of polymerisation. The results of this method were compared with those obtained by existing methods.

VI. The amylose content of rice starch during maturing. Motoji Taki. *Ibid.*, 1959, **33** (9), 778–781.—The method reported in Part V was applied to the determination of amylose in rice starch during maturing.

VII. The efficacy of amylose precipitants for the fractionation of amylose and amylopectin. Motoji Taki. *Ibid.*, 1959, **33** (9), 781–785.—The efficacy of nine kinds of amylose precipitant, *e.g.*, butanol and pentanol, was examined by a combination of the use of these reagents and determination by paper chromatography, as reported in Part V. The results showed n-pentanol and thymol to be the most satisfactory precipitants for the separation of both fractions. S. NATORI

638. **A new spot-test reaction for aldehydes.** V. Anger and G. Fischer (Loba-Chemie, Wien XIX, Austria). *Mikrochim. Acta*, 1960, (4), 592–596 (in German).—The red or pink colour produced by the reaction of indole with aldehydes is a useful spot test. The sensitivity is 1 μg or better except with chloral, isovaleraldehyde and glyoxal (10 μg) and glucose (20 μg). *Procedure*—Suspend pure indole (a few crystals) in 3 ml of conc. HCl. This reagent is colourless and stable for > 15 min. Add 5 drops to 1 drop of sample and warm. Compare the colour developed with a blank. J. P. STERN

639. **Sensitive new test for aliphatic, aromatic and heterocyclic aldehydes.** E. Sawicki and T. W. Stanley (R. A. Taft Sanitary Engng Center, U.S. Dept. of H.E. and W., Cincinnati 26, Ohio). *Mikrochim. Acta*, 1960, (4), 510–517 (in English).—Of 70 aldehydes tested, only chloral and hexadecanal failed to react with 2-hydrazinobenzothiazole (**I**) and *p*-nitrophenyldiazonium fluoroborate (**II**) to give a blue or green colour. Interference by excess of **I** is obviated by adding acetone (**III**) before **II**. The limits of sensitivity of the spot test are in the range 0·2 to 5 μg. The method is adaptable to colorimetry at 605 to 625 mμ and results are reproducible to within ± 10%. *Procedure*—For the spot-plate test, mix 1 drop each of 1% **I** in 1·3M-HCl and of the test soln. After 2 min. add 1 drop of **III** and, after a further minute, 1 drop of 1% aq. **II**. Set aside for 2 min., then add 1 drop each of 25% tetramethylammonium hydroxide and of **III**. A blue or green colour indicates the presence of an aldehyde (the blank is yellow).

J. P. STERN

640. **Quantitative estimation of low-boiling carbonyls by a modified α-oxoglutaric acid - 2,4-dinitrophenylhydrazone exchange procedure.** R. L. Stephens and A. P. Teszler (N. Carolina State Coll., Raleigh, U.S.A.). *Anal. Chem.*, 1960, **32** (8), 1047.—The method of Ralls (*Anal. Abstr.*, 1960, **7**, 4825) was modified to determine low-boiling carbonyls. Recoveries of acetaldehyde averaged 104·3 ± 3·5%. G. P. COOK

641. **Amperometric titration of aldehydes and ketones with 2,4-dinitrophenylhydrazine.** E. V. Zobov, Yu. S. Lyalikov and O. M. Mukhammednazarova. *Izv. Akad. Nauk TurkmenSSR*, 1959, (4), 45–50; *Ref. Zhur., Khim.*, 1960, (8), Abstr. No. 30,575.—In the amperometric titration of carbonyl compounds with a soln. of 2,4-dinitrophenylhydrazine (**I**), ultrasonic vibrations are used to obtain heavy precipitates of the hydrazones which will not interfere with the titration. The titration is carried out in a cell with parallel plane walls; one wall is ground to a thickness of 0·3 mm and to it is fixed with Canada balsam a silvered quartz plate with aluminium-foil contacts. The soln. is treated with ultrasonic vibrations for 0·5 min. after each addition of **I** soln. The optimum concn. of the **I** soln. is 0·005 to 0·05M; the **I** soln. are stable for 22 days. Aldehydes are satisfactorily determined at concn. of 0·001 to 0·04M. The method has been used to determine benzaldehyde and citral, and citral in the presence of β-irone and pseudo-β-irone. The mean error is ± 1·6%.

C. D. KOPKIN

642. **New spectrophotometric method for determination of formaldehyde.** Ummaid Singh Mahnot and N. C. Sogani (Chem. Dept., Gov. Coll., Ajmer). *J. Indian Chem. Soc.*, 1960, **37** (3), 185–188.—The reaction of formaldehyde with sulphanilic acid at pH 1·2 to 1·5 to afford a deep wine red, water-soluble compound, with an absorption peak at 480 mμ, is used as the basis for this determination. The system obeys Beer's law in the range 9 to 65 mg of formaldehyde per 100 ml of soln. The sensitivity of the colour reaction, determined in Nessler cylinders, is 1 part of formaldehyde in 4×10^4 parts of soln. The ratio of the reactants is 1:1. The molecular extinction coeff. at 480 mμ is 32·35, and the dissociation constant at 25° is $3{\cdot}69 \times 10^{-3}$.

I. JONES

643. **Gas-chromatographic determination of formaldehyde.** H. Kelker (Farbwerke Hoechst A.-G., Frankfurt/Main-Hoechst, Germany). *Z. anal. Chem.*, 1960, **176** (1), 3–8 (in German).—The sample (5 to 10 μl, giving an area on the recording graph < 6 sq. cm) is loaded on to a column (4·90 metres × 4·0 mm) containing Citroflex A8 (7·0 g) supported on Embacel. The mean temp. of the column is 122°. The column is eluted with H at a rate of 42·9 ml per min. For the quant. determination of formaldehyde, ethyl methyl ketone (in amount approx. that expected for formaldehyde) is added as an internal standard. Apart from a large excess of acetaldehyde, other organic liquids likely to be encountered do not interfere. The column may also be used for the qual. analysis of mixtures, the components being identified by their retention

vol. relative to benzene, other techniques (*e.g.*, i.r. spectrography or micro-analysis) being used only in cases of doubt. Retention vol. relative to benzene are tabulated for 42 compounds. J. H. WATON

644. **Gravimetric determination of formaldehyde and hexamine with dimedone.** H. Sluşanschi (Inst. f. landwirtschaftl. Forschung., Akad. R.P.R., Bucharest). *Z. LebensmittUntersuch.*, 1960, **112** (5), 390–391.—The temperatures previously specified for drying the formaldehyde - dimedone ppt. in this determination (Ionescu and Bodea, *Bull. Soc. Chim. France*, 1930, **47**, 1408; Spencer and Henshall, *Anal. Abstr.*, 1955, **2**, 373) are claimed to be too high, as this substance sublimes at 103°. The ppt. should be dried not above 100°, preferably in a vacuum oven. C. L. HINTON

645. **Continuous conductimetric determination of acetaldehyde.** I. A. Capuano (Union Carbide Olefins Co., Sth. Charleston, W. Va., U.S.A.). *Anal. Chem.*, 1960, **32** (8), 1025–1027.—The method is based on the conductimetric measurement of the H_2SO_3 produced by the Schiff's test for aldehydes. The mean deviation is $\pm$ 0·003% for concn. of 0·38% by vol. of added aldehyde and the recoveries are $> \simeq$ 95% in the 0·2 to 1·0% range. Details of the continuous-flow apparatus are given. G. P. COOK

646. **Separation of the long-chain fatty aldehydes by gas - liquid chromatography.** G. M. Gray (Lister Institute of Preventive Medicine, London, England). *J. Chromatography*, 1960, **4** (1), 52–59 (in English).—Long-chain fatty aldehydes are separated as aldehyde dimethyl acetals (details of preparation are given), with Apiezon L grease and Reoplex 400 as stationary phases. The relative retention volumes of some pure aldehyde dimethyl acetals and the corresponding fatty acid methyl esters are compared. E. C. BUTTERWORTH

647. **Separation of saturated and unsaturated C_4 and C_8 fatty acids by gas chromatography.** J. Janák, M. Dobiášová and K. Vereš (Lab. f. Gas Analysis, Czech. Acad. Sci., Brno). *Coll. Czech. Chem. Commun.*, 1960, **25** (6), 1566–1572 (in German).—Specific elution volumes are quoted for the methyl esters of various C_4 to C_8 fatty acids on Reoplex 400 (a polyoxypropylene glycol adipate), Silicone E301 and squalane at several temp., as well as for certain of the free acids on Reoplex 400. Typical chromatograms are illustrated, together with a graph showing the relationship between b.p. and elution data for methyl esters on Silicone E301 at 80°. H. M.

648. **Application of potassium manganate in quantitative analysis. VI. Determination of formic acid and the analysis of mixtures of formic, oxalic and acetic acids.** H. L. Polak (Lab. voor Anal. Scheikunde, Univ., Amsterdam, Netherlands). *Z. anal. Chem.*, 1960, **176** (1), 34–38 (in German).—Formic acid is accurately determined by oxidation with excess of MnO_4^{2-} in alkaline soln. for $\simeq$ 1 hr. at 60°, the unchanged reagent being back-titrated iodimetrically in acid soln. The time is reduced if a known amount of $KMnO_4$ is added towards the end of the oxidation. In a third modification H_2TeO_4 is added, and the excess of MnO_4^{2-} is titrated potentiometrically with As^{III} soln. Total formic and oxalic acids are determined by oxidising with MnO_4^{2-}, first in alkaline soln., and then in acid soln.; formic acid alone is then oxidised in alkaline soln. In both cases the excess of MnO_4^{2-} is determined iodimetrically. Acetic acid does not interfere. J. H. WATON

649. **Colorimetric determination of citric and malic acids.** V. I. Kriventsov. *Trudy Inst. Khim., Akad. Nauk TurkmenSSR*, 1959, **1**, 32–51; *Ref. Zhur., Khim.*, 1960, (11), Abstr. No. 42,469.—A method is described for determining citric (**I**) and malic (**II**) acids when they are present together, as in cotton waste [*Ref. Zhur., Khim., Biol. Khim.*, 1960, (8), Abstr. No. 11,554]. Extract **I** and **II** from the sample (5 g) (Yermakova *et al.*, *Metody Biokhim. Issled. Rastenii, Moskva, Sel'khozgiz*, 1952) and oxidise and brominate an aliquot of the extract by the addition of soln. of KBr, H_2SO_4 and $KMnO_4$. Cool, extract the pentabromoacetone (**III**) formed from **I** with light petroleum, add Na_2S soln. and determine the yellow reaction product photometrically. Steam-distil off the glyoxal formed in the oxidation of **II** from an aliquot of the aq. soln. remaining after the extraction of **III**, treat with aq. 2,4-dinitrophenylhydrazine hydrochloride soln., filter off, and wash the hydrazone with dil. HCl, dissolve it in 2% methanolic NaOH soln., add 3% methanolic Na_2S soln. and measure the violet soln. photometrically with a green filter. K. R. COOK

650. **Organic chemical microscopy. VIII. Dibenzofuran-2-sulphonic acid salts of amines in qualitative organic analysis.** R. E. Dunbar and F. J. Ferrin (N. Dakota State College, Fargo, U.S.A.). *Microchem. J.*, 1960, **4** (2), 167–179.—Dibenzofuran-2-sulphonic acid (**I**) is a strong acid easily crystallised from cold H_2O to give a stable product (m.p. 147° to 147·5°). It forms derivatives with most amines, which can be identified by m.p. and crystalline form; analytical data and photomicrographs are given for 31 amine derivatives. *Preparation of* **I**—Heat 67 g of dibenzofuran with 97 g of 96% H_2SO_4 on a steam bath for 1 hr. Pour into 300 ml of H_2O and store at 0° for several hours. Filter, and recrystallise **I** from boiling H_2O. P. D. PARR-RICHARD

651. **Gas chromatography of high-molecular-weight fatty primary amines.** J. Nelson and A. Milun (General Mills, Inc., Minneapolis, Minn., U.S.A.). *Chem. & Ind.*, 1960, (23), 663–664.—The chain-length of high-molecular-weight fatty primary amines has been determined by chromatographing their mixtures on either silicone grease on sodium chloride or silicone oil on potassium hydroxide treated with Chromosorb W. Two typical chromatograms are presented. S. M. MARSH

652. **Gas - liquid chromatography of fatty derivatives. III. Analysis of fatty amines.** W. E. Link, R. A. Morrissette, A. D. Cooper and C. F. Smullin (Archer-Daniels-Midland Co., Minneapolis, Minn.). *J. Amer. Oil Chem. Soc.*, 1960, **37** (7), 364–366.—The separation and quant. determination of C_8 to C_{22} saturated fatty amines has been carried out with silicone grease and Apiezon L on Chromosorb and Chromosorb W, respectively. The support was specially pre-treated with 2 to 5% methanolic KOH to overcome adsorptivity and prolong the column life. Good separation and high accuracy were achieved at 225°. The relative response of primary alkyl fatty amines was a linear function of mol. wt. P. M. KINGSTON

653. **Colorimetric reactions of 3,5-dinitro-o-toluamide and related compounds with aliphatic diamines.** G. N. Smith and M. G. Swank (Dow Chemical Co., Midland, Mich., U.S.A.). *Anal. Chem.*, 1960, **32** (8), 978–981.—The reactions can be used to determine and distinguish 3,5-dinitro-*o*-toluamide and its related compounds. The complexes formed exhibit absorption peaks in the visible region. The factors that influence the formation of the complexes are discussed. G. P. Cook

654. **Thermogravimetric and differential thermal analysis of ethylenedinitrilotetra-acetic acid and its derivatives.** W. W. Wendlandt (Dept. of Chem., Texas Technol. College, Lubbock, U.S.A.). *Anal. Chem.*, 1960, **32** (7), 848–850.—The free acid and derivatives all decompose between 153° and 265°. The salts lose weight at lower temp. because of the evolution of hydrate-bound water.

K. A. Proctor

655. **Gas-chromatographic analysis of nitriles.** I. Lysyj (Food Machinery and Chem. Corp., Princeton, N.J., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 771.—The basis of the method is that the order of elution of nitriles on a non-polar column is different from that on a polar one. By using both systems in conjunction, a mixture of acrylo-, aceto-, methacrylo- and propio-nitriles was analysed with a max. error of $\simeq 5\%$. G. P. Cook

656. **Determination of primary nitroparaffins by the nitrous acid reaction.** A. P. Altshuller and I. R. Cohen (R. A. Taft San. Engng Center, Cincinnati, Ohio, U.S.A.). *Anal. Chem.*, 1960, **32** (7), 881–882.—Potassium hydroxide (1 g) is added to an aq. soln. of the sample (2 ml), which is then treated with KNO_2 (0·25 g) and 18N-H_2SO_4 (0·6 ml). The soln. is extracted with ethyl ether (10 ml), which is in turn extracted with water (3 ml) containing satd. NaOH soln. (4 to 5 drops). The extinction of the aq. phase is measured at 330 mμ. The extinction coeff. of interfering aliphatic nitro-compounds are tabulated. G. P. Cook

657. **Analysis of the products of nitration of methane in the gas phase. Determination of nitromethane in the presence of nitrite.** J. Giber and T. Meisel (Dept. Ind. Org. Chem., Tech. Univ., Budapest). *Acta Chim. Acad. Sci. Hung.*, 1960, **22** (4), 435–441 (in English).—From the mixture of products obtained on the nitration of methane, the portion condensing at −70° is collected and the frozen material is dissolved in H_2O made alkaline to pH 10. The nitromethane is oxidised to nitrite with an alkaline soln. of H_2O_2, the excess of which is decomposed by boiling. The nitrite is determined colorimetrically by diazotisation with sulphanilic acid and coupling with hydroxynaphthoic acid. The extinction of the dye is measured in a Pulfrich photometer with a green filter, and is independent of pH in the range of 10 to 14; Beer's law is obeyed for 0·1 to 20 μg of nitrite per ml. If nitrite is present in the reaction mixture, the method is applied before and after oxidation of the nitromethane, which is calculated by difference. Alternatively, large amounts of nitrite are decomposed with urea before the oxidation stage. The relative error is $\pm 3\%$, and the sensitivity 0·1 μg per ml. G. P. Cook

658. **Micro-determination of 2,2-dinitropropane by zinc amalgam reduction to nitrite.** Fujiko Shinozuka and J. T. Stock (Univ. Connecticut, Storrs, U.S.A.). *Anal. Chem.*, 1960, **32** (7), 883–884.—2,2-Dinitropropane can be determined alone or in admixture with 2-nitropropane by reduction with zinc amalgam at a controlled pH. The liberated NO_2^- are measured absorptiometrically at 520 mμ. Recoveries are $\simeq 100\%$. G. P. Cook

659. **Determination of sodium sulphide and mercaptans [thiols] in the presence of each other.** M. Wroński (Dept. of Chem. Technol., Univ. of Łódź, Poland). *Analyst*, 1960, **85**, 526–527.—For determining alkali sulphide plus thiol in soln., 5 ml of N-aq. NH_3 and 1 ml of 0·02% (w/v) thiofluorescein soln. are added, and the mixture is diluted to 100 ml with water containing $\simeq 0{\cdot}1\%$ of Na_2SO_3. The liquid is then titrated with 0·001 to 0·05N-*o*-hydroxymercuribenzoic acid until the blue colour is discharged. To a soln. of alkali sulphide and thiol, 5 ml of N-aq. NH_3 and a methanolic soln. of vinyl cyanide (to remove the thiol) are added and, after 2 to 15 min. (according to the dilution and the amount of thiol present), the liquid is diluted to 100 ml and titrated as before. Ethanethiol, thioglycollic acid and cysteine can be determined similarly in the presence of sulphide. If sulphide, thiol and cyanide are present, the cyanide and sulphide plus thiol are determined as previously described for sulphide plus cyanide (*Ibid.*, 1959, **84**, 668), and in a third sample, after the thiol has been removed with vinyl cyanide and cyanide with formaldehyde, the sulphide alone is titrated with *o*-hydroxymercuribenzoic acid, a soln. of dithizone in NaOH soln. being used as indicator. There is no interference from SO_3^{2-}, $S_2O_3^{2-}$ or SCN^-.

A. O. Jones

660. **Simultaneous determination of hydrogen sulphide and mercaptans [thiols] by potentiometric titration.** M. W. Tamele, L. B. Ryland and R. N. McCoy (Emeryville Res. Center, Shell Devel. Co., Calif., U.S.A.). *Anal. Chem.*, 1960, **32** (8), 1007–1011.—The method is based on the potentiometric titration of mixtures of H_2S and thiols with $AgNO_3$ soln., a silver wire coated with Ag_2S being used as the indicator electrode. Aq. samples are titrated in NaOH soln. containing aq. NH_3 and samples that are insol. in the aq. electrolyte are titrated with alcoholic $AgNO_3$ soln. in alcoholic Na acetate soln. Silver sulphide is pptd. first at a high negative potential and a marked change in potential occurs when pptn. is complete. The pptn. of the silver mercaptide begins at a lower potential, and at the completion of pptn. another marked change in potential occurs. Elementary S interferes, but can be removed. The error is $< 1\%$.

G. P. Cook

661. **Determination of basicity of substituted phosphines by non-aqueous titrimetry.** C. A. Streuli (Central Res. Div., American Cyanamid Co., Stamford, Conn., U.S.A.). *Anal. Chem.*, 1960, **32** (8), 985–987.—The relative basicity of a number of substituted phosphines has been established by titrations in nitromethane and methanol - water solvents. The results indicate that tertiary alkyl phosphines are the strongest bases and that aryl and negatively substituted compounds decrease in basic strength. K. A. Proctor

662. **Micropyrolytic - gas-chromatographic technique for the analysis of organic phosphates and thiophosphates.** C. E. Legate and H. D. Burnham (Wood River Res. Lab., Shell Oil Co., Ill., U.S.A.). *Anal. Chem.*, 1960, **32** (8), 1042–1045.—In

the technique described, which can be used for the identification of organic radicals in organic phosphates and thiophosphates, especially zinc dialkyl thiolothionates, the compound is pyrolysed in the inlet system of a gas chromatograph, and the separated pyrolysis products are collected for identification by mass or i.r. spectrometry. An inlet system suitable for pyrolysis or for conventional vaporisation is described. K. A. PROCTOR

663. **Analysis of organosilicon compounds with special reference to silanes and siloxanes. A review.** J. C. B. Smith (Midland Silicones Ltd., Barry, Glamorgan, Wales). *Analyst*, 1960, **85**, 465–474.—The manufacture of organosilicon compounds is briefly described. Procedures for their analysis are reviewed, including methods based on the determination of elementary Si, methods for the analytical control of substituted chlorosilanes (intermediates in the manufacture of silicones) by infra-red spectroscopy, fractional distillation and gas - liquid chromatography. Physical and chemical methods for the determination of side-groups and for the analysis of polymers are reviewed. (62 references.) A. O. JONES

664. **Gas-chromatographic separation and identification of silicon compounds.** G. Fritz and D. Ksinsik (Anorg.-chem. Inst., Univ., Münster). *Z. anorg. Chem.*, 1960, **304** (5–6), 241–248.—The chlorosilanes could not be separated by gas adsorption chromatography on any of the usual solid adsorbents. By gas - liquid partition chromatography, quantitative separation of the lower-boiling silicon compounds was achieved on a column containing silicone oil DC 200/350 and dibutyl phthalate on kieselguhr (3:1:5, by wt.) at 30° and 60°, with H as carrier gas, and of the higher-boiling compounds on a column containing silicone oil on kieselguhr (3:10) at 150°. G. BURGER

665. **Determination of the crystallisation-point of pure benzene.** German Standard DIN 51798. *Erdöl u. Kohle*, 1960, **13** (7), 493.—Directions are given for the determination of the freezing-point, which is carried out on a water-saturated sample, a correction being applied for the water. N. E.

666. **Rapid colorimetric determination of 1 p.p.m. of thiophen in benzene. Use of permanent colour standards.** H. A. Barnett, C. E. Bole and C. F. Glick (U.S. Steel Corp., Monroeville, Pa., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 842–844.—The isatin method was modified. The need for a spectrophotometer can be eliminated by reference to a simple block comparator containing a series of artificial colour standards prepared from soln. of isatin, chlorophenol red and Indian ink. The maximum error was ± 0·1 p.p.m. when the standards were less than 2 months old. G. P. COOK

667. **Infra-red spectra of monoalkylbenzenes.** J. C. Hawkes and A. J. Neale (Monsanto Chemicals Ltd., Ruabon, N. Wales). *Spectrochim. Acta*, 1960, **16** (6), 633–653.—Infra-red spectra of 42 monoalkylbenzenes have been determined.

668. **Determination of aromatic chloro-derivatives.** V. A. Kulik. *Gigiena Truda i Prof. Zabolevaniya*, 1959, (5), 54; *Ref. Zhur., Khim.*, 1960, (8), Abstr. No. 30,574.—Chlorobenzene or other aromatic chlorine derivative is nitrated at 100° for 30 min. and, after cooling, the mixture is diluted to a known vol. and the extinction of the soln. is measured on photometer FEK-M with a blue filter. In alkaline medium the sensitivity of the method is increased by 70 to 100%. With low concn. of the material in air, 3 to 4 litres of the air is drawn through two absorbing tubes containing porous plate at a rate of 5 to 6 litres per hr. Mono-, di- and tri-chlorobenzenes can also be determined by nitration and subsequent reduction at the dropping-mercury cathode. C. D. KOPKIN

669. **Light-absorption studies. XVII. The ultraviolet absorption spectra of chlorobenzenes.** W. F. Forbes (Div. Protein Chem., C.S.I.R.O., Victoria, Australia). *Canad. J. Chem.*, 1960, **38** (7), 1104–1112.—The u.v. absorption spectra of chlorobenzene and ten substituted derivatives are given in detail.

670. **Chromatographic separation of derivatives of phenol on cation-exchange resins.** Tokuichiro Seki (Dept. of Genetics, Osaka Univ. Med. Sch., Japan). *J. Chromatography*, 1960, **4** (1), 6–10 (in English).—In the chromatographic separation of phenol derivatives, Amberlite IR-112 or Duolite C25 is used as the adsorbent and the following solvents as eluents—(*a*), (*b*) and (*c*) citrate buffer (pH 4·0) (1 litre) containing, respectively, benzyl alcohol (25 ml), ethyl methyl ketone (250 ml) and ethanol (250 ml); (*d*) methanol - ethanol - 0·1N-HCl (1:3:4); (*e*) $NaHCO_3$ (9·3 g), Na_2CO_3 (8·5 g) and EDTA (0·50 g of disodium salt) dissolved in water to 1 litre (pH 9·70 ± 0·02); and (*f*) $NaHCO_3$ (4·2 g), Na_2CO_3 (3·1 g) and EDTA (0·25 g of disodium salt) dissolved in water to 1 litre (pH 9·65 ± 0·02) with ethanol (200 ml) added. Isomers of mononitrophenols can be separated on a column of Amberlite IR-112 with solvent (*a*), isomers of dihydroxybenzenes on Duolite C25 with solvent (*c*), polynitrophenols on Duolite C25 with solvent (*b*), isomers of cresol on Amberlite IR-112 with solvent (*e*) and *m*-cresol can be separated from other cresols on Duolite C25 with solvent (*f*). Quinol, catechol, phenol, *p*-cresol and *p*-butylphenol are separated on a column of partially esterified Amberlite IRC-50 (prep. described) with solvent (*d*).
E. C. BUTTERWORTH

671. **Acid-catalysed acetylation. Determination of phenols, thiols, amines, and mixtures.** G. H. Schenk and J. S. Fritz (Iowa State Univ., Ames, U.S.A.). *Anal. Chem.*, 1960, **32** (8), 987–990.—Phenols, thiols and amines can be determined by titration with NaOH soln. after their $HClO_4$-catalysed acetylation in ethyl acetate. Sterically hindered phenols can be determined after reaction for only 5 min. at room temp. Sterically hindered phenols and negatively substituted aromatic amines react more slowly in pyridine and in soln. containing less $HClO_4$, and therefore, by suitable choice of conditions, simple phenols and aromatic amines can be determined in the presence of hindered phenols and less reactive amines. Recoveries of about 97 to 105% are obtained for the determination of 4-methoxyphenol in the presence of a number of hindered phenols, and the reproducibility is within ± 1% for the analysis of pure compounds. G. P. COOK

672. **Some new alkylguaiacols and a new method of chromatographic identification of phenols.** E. Fedeli, A. Fiecchi and G. Jommi (Univ., Milano, Italy). *Gazz. Chim. Ital.*, 1959, **89** (3), 824–833.—The chromatography of the 4-nitrophenylazo-derivatives (prep. described) of substituted and unsubstituted phenols and guaiacols is carried out

on Whatman No. 3 paper by the ascending technique at 15°, with 0·005 ml of a soln. of the derivative in $CHCl_3$ (1 to 2 μg per ml). The solvent systems employed (all saturated with n-butanol) are—0·1N-NaOH - 0·1M-borate (7:3) and 0·5N-, 0·1N-, 0·05N- and 0·033N-NaOH. The R_F values are tabulated for 21 compounds, and depend, in a general way, on the positions of the substituents in the aromatic nucleus. The paper chromatography of the 2,4-dinitrophenylhydrazones of aromatic hydroxyaldehydes and hydroxyketones with 0·05N-NaOH satd. with n-butanol is also described and R_F values are tabulated for 8 compounds.

R. E. E.

673 **Paper chromatography of bisphenol A.** G. Challa and P. H. Hermans (Inst. Cellulose Res., Utrecht, Holland). *Anal. Chem.*, 1960, **32** (7), 778–779.—The main constituent [2,2-di-(4-hydroxyphenyl)propane] and the three principal impurities of commercial bisphenol A were separated by one-dimensional paper chromatography in an atmosphere of NH_3 with a mixture of n-propanol and kerosine (9:11) as the eluent. With fairly pure samples the impurities were preconcentrated by fractional vacuum sublimation at 95° and 1 torr. With commercial samples the method gave purity results which agreed with freezing-point-depression values.

G. P. Cook

674. **Determination of 1-(*p*-bromophenyl)-1-phenylethanol [α-methyl-*p*-bromobenzhydrol] and 1,1-diphenylethanol [α-methylbenzhydrol].** B. Buděšínský and M. Aixnerová (Res. Inst. Pharm. and Biochem., Prague). *Českosl. Farm.*, 1960, **9** (6), 312–313.—The method is based on the dehydration of α-methyl-*p*-bromobenzhydrol or α-methylbenzhydrol and the bromimetric determination of the ethylene derivative formed. *Procedure*—Dissolve 1 to 2 milli-equiv. of the sample in 10 ml of pyridine - acetic anhydride (3:1) and boil for 90 min. under reflux. Cool, wash the condenser with $CHCl_3$ (10 ml) and to the cold mixture add 0·1N-Br in glacial acetic acid (25 ml). Stopper the flask, set aside in darkness for 5 min., then add KI (1 g) and H_2SO_4 (20%) (10 ml); dilute with H_2O (50 ml) and titrate with 0·1N-$Na_2S_2O_3$, with starch as indicator. Carry out a blank. The error is ≯ − 0·95%. Ethylene derivatives, if present, are determined before dehydration; acetophenone and *p*-bromoacetophenone do not interfere.

J. Zýka

675. **Paper chromatography of 2,4-dinitrophenylhydrazones of aromatic ketones.** E. Breuer, H. Leader and S. Sarel (Hebrew Univ. Sch. of Pharm., Jerusalem, Israel). *Bull. Res. Council Israel, A*, 1960, **9** (1–2), 43–45.—Separation of the 2,4-dinitrophenylhydrazones of alkyl aryl, cycloalkyl aryl and diaryl ketones was effected on Whatman No. 1 paper by using H_2O - dimethylformamide as the stationary phase and cyclohexane - CCl_4 - dimethylformamide (20:4:1) as the mobile phase. The R_F values for eight ketones and three aldehydes are given.

G. P. Cook

676. **Detection of polynuclear diaryl ketones: application to air pollution.** T. W. Stanley (Robert A. Taft Sanitary Engng Center, U.S. Dept. of Health, Educ. and Welfare, Cincinnati, Ohio). *Chemist Analyst*, 1960, **49** (2), 47, 56.—Methylmagnesium bromide in ethyl ether is added to a soln. of the sample in benzene and the soln. is evaporated to dryness. The residue is dissolved in 10% HCl and extracted with ethyl ether. The ether extract is evaporated to dryness and trifluoroacetic acid is added. Stable colours are formed, ranging from red to blue. The reaction can be used as a spot test, or for spectrophotometric determinations. The test described is specific for diaryl ketones, except that 2-benzoylthiophen gives a green colour.

G. Burger

677. **Infra-red analysis of various phenoxyacetic acids.** F. J. Witmer, D. N. Thomas and J. B. Vernetti (Chipman Chem. Co., Portland, Ore.). *Anal. Chem.*, 1960, **32** (7), 887–888.—Results are given for phenoxyacetic acid and 15 chloro-derivatives.

678. **Photometric titration of aromatic amines.** C. A. Reynolds, F. H. Walker and E. Cochran (Univ. of Kansas, Lawrence, U.S.A.). *Anal. Chem.*, 1960, **32** (8), 983–984.—The amines are directly titrated with acetic anhydride in pyridine at wavelengths in the 310 to 370-mμ range; the most suitable wavelength for each amine is previously determined. The extinction is measured as a function of the vol. of the standard acetylating reagent. The precision is within 0·8%. The method is applicable to unsubstituted amines or those substituted with alkyl, alkoxyl, hydroxyl or halogen groups.

G. P. Cook

679. **Analysis of mixtures of *N*-ethylaniline and *N*-ethyl-*N*-2-hydroxyethylaniline.** K. B. Whetsel, W. E. Roberson and M. W. Krell (Tennessee Eastman Co., Kingsport, Tenn.). *Anal. Chem.*, 1960, **32** (7), 888.—Infra-red data are given.

680. **Detection of diphenylamine and its derivatives in spot-test analysis.** F. Feigl and D. Goldstein (Min. da Agric., Rio de Janeiro, Brazil). *Anal. Chem.*, 1960, **32** (7), 861–862.—The sample is heated with hydrated oxalic acid at 160°. The temp. is then raised to 180° to 190°. The presence of diphenylamine and its derivatives is indicated by the development of a blue colour within a few minutes. The limits of detection for 15 compounds are given. Carbazole and its derivatives also respond.

G. P. Cook

681. **Analysis of mixtures of *m*-toluidine and *N*-ethyl-*m*-toluidine.** K. B. Whetsel, W. E. Roberson and M. W. Krell (Tennessee Eastman Co., Kingsport, Tenn.). *Anal. Chem.*, 1960, **32** (7), 888.—Infra-red data are given.

682. **Spot-test detection and differentiation of *o*- and *p*-nitrophenol.** F. Feigl and D. Haguenauer (Lab. da Prod. Mineral, Min. da Agric., Rio de Janeiro, Brazil). *Chemist Analyst*, 1960, **49** (2), 43–44.—A small sample is heated to 120° in a micro test-tube the mouth of which is covered with a filter-paper moistened with dil. NaOH or Na_2S soln. A yellow or orange colour indicates the presence of *o*-nitrophenol. Another sample is heated to 120° with solid $Na_2S_2O_3.5H_2O$. The cooled melt is dissolved in water and shaken with benzene. A yellow aq. layer indicates the presence of *p*-nitrophenol. The limits of detection are 1·5 μg and 2·5 μg for the *o*- and *p*-isomers, respectively. If the sample is a soln. it should be evaporated before testing.

G. Burger

683. **Chromatography of dyestuff intermediates. XI. Chromatographic separation and identification of the naphthalenesulphonic acids.** J. Latinák

(Východočeské Chem. Závody-Synthesia, Pardubice-Semtín). *Coll. Czech. Chem. Commun.*, 1960, **25** (6), 1649–1655 (in German).—R_F values are quoted for 12 naphthalenesulphonic acids in the systems HCl - H_2O (1:3) and n-propanol - aq. NH_3 (2:1), on S. & S. paper No. 2043a. The traces are rendered visible by spraying with pinakryptol yellow and viewing in u.v. light. Two-dimensional chromatography by the ascending method is necessary for separation of certain pairs, only the 2,6- and 2,7-disulphonic acids being incapable of resolution. If, however, these are converted into the corresponding phenols by fusion with NaOH, they may then be separated on paper impregnated with $NaHCO_3$ soln., with n-propanol - aq. $NaHCO_3$ soln. as solvent. Diazotised *p*-nitroaniline is used as the spray reagent. H. M.

684. **Bromimetric determination of β-naphthoxyethanol [2-(2-naphthyloxy)ethanol].** F. Buben and F. Jančík (Res. Inst. Pharm. and Biochem., Prague). *Českosl. Farm.*, 1960, **9** (6), 307–309.—Conditions were found for the formation of the derivative 1-bromo-2-naphthyloxyethyl acetate, and the reaction was used for potentiometric determination. When determining 2-(2-naphthyloxy)ethanol (**I**) in Anavenol, which contains 5-allyl-5-cyclohexenyl-2-thiobarbituric acid, the **I** must be first separated by extraction. *Procedure for* **I**—Dissolve the sample (150 mg) in glacial acetic acid (25 ml), add conc. HCl (1 ml) and KBr (1 g) and titrate potentiometrically (platinum and S.C.E. electrodes) with 0·1N-$KBrO_3$. The mean error is $\pm$ 0·3%. *Procedure with Anavenol*—To 1 ml of the injection soln. in a separating-funnel add H_2O (20 ml) and 2N-NaOH (2 ml) and extract with 15, 10, 10, 10 and 5 ml of $CHCl_3$. Evaporate the combined extracts, dissolve the residue in glacial acetic acid (25 ml) and proceed as described above.

J. Zýka

685. **Determination of J-acid-urea [6,6′-di-(1-hydroxy-3-sulphonaphthyl)urea].** M. Matrka and F. Navrátil (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Průmysl*, 1960, **10** (7), 361–362.—The method is based on alkaline hydrolysis and diazotisation titration of the resulting 6-amino-1-naphthol-3-sulphonic acid (J-acid). *Procedure*—Dissolve the sample (5·04 g), after the addition of Na_2CO_3, in H_2O and dilute to 100 ml with H_2O. To a 10-ml aliquot add 2·5N-NaOH (25 ml) and boil under reflux for 3 hr. Transfer the soln. into Na *m*-xylenesulphonate soln. (40%) (100 ml) and add conc. HCl till the reaction with Congo red as indicator becomes positive. Titrate with 0·1N-$NaNO_2$ at 20°, with starch - KI paper as indicator, or potentiometrically. J. Zýka

686. **Identification of organic compounds. XXXVI. Paper-chromatographic separation and identification of aminoanthraquinones.** J. Gasparič (Forschungsinst. für organ. Synthesen, Pardubice-Rybitví, Czechoslovakia). *J. Chromatography*, 1960, **4** (1), 75–79 (in German).—Whatman paper No. 3 impregnated with 1-bromonaphthalene or formamide and solvent systems pyridine - water (1:1 or 2:1), toluene or $CHCl_3$ are used to separate aminoanthraquinones. The colours of the spots and the R_F values of 37 aminoanthraquinones in these systems are tabulated. E. C. Butterworth

687. **Analysis of isomeric terphenyls by infra-red spectroscopy.** C. A. Ceselli and M. Camia (Ist. "G. Donegani," Soc. Montecatini, Novara). *Chim. e Ind.*, 1960, **42** (7), 721–724.—The method is described. Graphs of extinction *vs.* concn. are plotted for *o*-, *m*- and *p*-terphenyl, with bands at 11·92, 12·52 and 12·87 μ; full i.r. spectra are illustrated, and the results obtained on a series of synthetic mixtures are given. C. A. Finch

688. **Analysis of terpene hydrocarbons and related compounds by gas chromatography.** W. J. Zubyk and A. Z. Conner (Hercules Powder Co., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1960, **32** (8), 912–917.—Carbowax 4000 and didecyl phthalate are used as stationary liquid phases with dichloromethane and ethyl ether, respectively, as the solvents. Relative retention data for 44 compounds are given. In the analysis of monocyclic and bicyclic mixtures the results showed max. deviations from the true value of 1 or 2% absolute. Good agreement was attained with the results by i.r. analysis of crude wood turpentine and α-pinene hydration products.

G. P. Cook

689. **The infra-red spectra of polycyclic heteroaromatic compounds. I. Monosubstituted quinolines.** A. R. Katritzky and R. A. Jones (Univ. Chem. Lab., Cambridge, England). *J. Chem. Soc.*, 1960, 2942–2947.—The bands characteristic of 8 monosubstituted quinoline nuclei are established.

N. E.

690. **Gas chromatography of nitrogen-containing heterocyclic compounds. I. Separation and analysis of quinoline and higher pyridine bases as well as indoles by gas - liquid chromatography.** J. Janák and M. Hřivnáč (Lab. f. Gas Analysis, Czech. Acad. Sci., Brno). *Coll. Czech. Chem. Commun.*, 1960, **25** (6), 1557–1565 (in German).—Reoplex 400 (a polyoxypropylene glycol adipate) is suggested as a stationary phase for the separation of the compounds named, and a theory based on their electronic configuration is proposed to explain the differences in elution characteristics. Specific elution volumes are quoted for 22 heterocyclic bases on Reoplex 400, Apiezon L and Silicone E301 at 200°, as well as for 10 aromatic compounds accompanying these bases in coal tar. Examples are given of chromatograms from technical mixtures isolated from coal tar. H. M.

691. **Thermal properties of quinolinium molybdophosphate.** W. W. Wendlandt and W. M. Hoffman (Dept. of Chem., Texas Technol. Coll., Lubbock, U.S.A.). *Anal. Chem.*, 1960, **32** (8), 1011–1012.—From investigations of its thermal properties it has been shown that quinolinium molybdophosphate can be safely dried to constant weight in the 150° to 300° range. K. A. Proctor

692. **Separation and micro-determination of hexahydro-1,3,5-trinitro-sym.-triazine [RDX] in octahydro-1,3,5,7-tetranitro-sym.-tetrazine [HMX]. Use of paper partition chromatography.** S. K. Yasuda and R. N. Rogers (Univ. Calif., Los Alamos, N.M., U.S.A.). *Anal. Chem.*, 1960, **32** (8), 910–911.—About 10 to 40 μl of a 1% soln. of the sample in acetone is applied to the paper strip [Whatman 3MM paper that has been washed with 1,2-dichloroethane, then immersed in a 50% (v/v) soln. of formamide in acetone, and air-dried], and the RDX is eluted with 1,2-dichloroethane for about 2 hr. The RDX in the eluate is decomposed by H_2SO_4 to formaldehyde, which is determined by the chromotropic acid procedure. Recoveries are > 95%.

G. P. Cook

693. **New separations of sulphur heterocyclic compounds by gas-liquid chromatography.** M. Hřivnác and J. Janák (Lab. for Gas Analysis, Czech. Acad. Sci., Brno). *Chem. & Ind.*, 1960, (29), 930.—Mixtures such as benzene - thiophen - toluene and naphthalene - thionaphthen - 2-methylnaphthalene can be separated on columns of 30% (w/w) of Reoplex 400 (polyoxypropylene glycol adipate) on Celite 545 at temp. up to about 200° with a hydrogen flow rate of ≃ 1 ml per sec. The column length varies from 0·9 to 1·6 metres. The retention volumes are sufficiently different to allow technical grades of benzene and naphthalene to be examined for their content of sulphur impurities on quite short columns. K. A. PROCTOR

694. **Thiazoles. IV. Proton magnetic resonance spectra of thiazole and its methyl derivatives.** A. Taurins and W. G. Schneider (Chem. Dept., McGill Univ., Montreal, Canada). *Canad. J. Chem.*, 1960, **38** (7), 1237–1239.—The spectra of thiazole, 2- and 4-methylthiazole and 2:4-dimethylthiazole are studied. N. E.

695. **Characterisation of petroleum nitrogen compounds by selective acetylation and non-aqueous titration.** S. W. Nicksic and S. H. Judd (Calif. Res. Corp., Richmond, U.S.A.). *Anal. Chem.*, 1960, **32** (8), 998–1002.—The method is based on the acetylation of nitrogen bases in glacial acetic acid. The primary and secondary amines are converted into substituted acetamides, which can no longer be titrated with $HClO_4$. The rate of acetylation can then be followed by periodically titrating a portion from the reaction medium. Tertiary amines are not acetylated, so that the residual titration after complete acetylation is a measure of the tertiary amine content. Differences in the rates of acetylation enable some nitrogen compounds in petroleum to be characterised. G. P. COOK

696. **High-frequency titrimetric determination of hydrogen sulphide and thiols in technical gases after absorption in alkaline solution.** F. Oehme (Weilheim/Obb., Marienplatz 8, Germany). *Erdöl u. Kohle*, 1960, **13** (6), 394–396.—The alkaline (30% NaOH) soln. containing the sulphur compounds is passed through an acid ion-exchange column which replaces Na^+ with H^+, and the liberated H_2S and thiols are titrated conductimetrically with 0·1 or 0·01N-Pb acetate in a high-frequency capacitative cell. The ppt. is centrifuged and washed, and warmed with a measured volume of collidine or picoline, which dissolves the lead mercaptides; PbS is removed by centrifuging and the concn. of mercaptide is determined colorimetrically from an extinction graph given by a pure thiol (butanethiol was used). Correction should be made for the change of concn. due to the replacement of NaOH by H_2O. A. R. PEARSON

697. **Determination of mercaptans [thiols] in naphthas by low-voltage mass spectrometry.** W. P. Hoogendonk and F. W. Porsche [Tech. Service Lab., Standard Oil Co. (Indiana), Whiting, U.S.A.]. *Anal. Chem.*, 1960, **32** (8), 941–942.—The method described can be used to determine alkylthiols containing up to 7 carbon atoms. After extraction from chilled naphtha with K isobutyrate soln., the thiols are concentrated into 1 ml of iso-octane and analysed with a mass spectrometer modified for operation at low ionising voltages. The method should be applicable, with modifications, to the determination of other thiols. K. A. PROCTOR

698. **Quantitative determination of tetraethyllead in commercial petrol.** A. Blumenthal (Chem. Lab. der Stadt, Zürich). *Mitt. Lebensmitt. Hyg., Bern*, 1960, **51** (3), 159–165 (in German).—New additives to improve the quality of petrol have made the usual method, in which the sample is treated with H_2SO_4, unsatisfactory. The direct and indirect iodimetric methods and a complexometric method were compared. Analytical details and results are given. The direct complexometric titration of the extracted $PbCl_4$ in the presence of tartrate was the most accurate. I. DICKINSON

699. **Carbon-type analysis of lubricating oil. Significance of pure compound data.** R. W. King, M. A. Kust and S. S. Kurtz, jun. (Sun Oil Co., Marcus Hook, Pa., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 738–745.—Several methods were evaluated by using data for pure compounds of high mol. wt. synthesised by API Res. Proj. 42. The study showed that the correlations at present available for determining the carbon-type composition of lubricating oil give, in general, satisfactory agreement with the data for pure compounds. The data for multicyclic aromatics do not agree well with the correlations for petroleum fractions. This would appear to show that these compounds are mainly of the condensed variety, in agreement with the results of API Res. Proj. 6 for such materials. G. P. COOK

700. **Benzene from brown-coal light oil. I. Benzene content of brown-coal light oils and fractions of high-temperature medium-pressure 'HTM' process.** R. Mahrwald, E. Hüttig, R. Schwerdt and M. Wagner (VEB Hydrierwerk, Zeitz, Germany). *Chem. Tech., Berlin*, 1960, **12** (5), 266–272.—The benzene contents of brown-coal light oils, and of raw- and end-products in the H.T.M. process, were determined by i.r. spectroscopy, gas chromatography, the fluorescence indicator - adsorption process, and the measurement of sp. dispersion. I.r. spectroscopy is the most useful of these methods. E. M. MAYES

701. **Application of gas chromatography to the analysis of ammonia synthesis gases.** J. Lacy, K. G. Woolmington and R. V. Hill. *S. Afr. Ind. Chem.*, 1960, **14** (3), 47–51.—Apparatus and procedures are described for the analysis of the gas streams obtained during plant operation. A 6-ft. U-shaped column packed with active carbon, with differential thermal-conductivity detection, is used for the determination of N, H and CO in "semi-water gas" with Ar as carrier, and of H, Ar and methane in "circulating gas" with N as carrier. The determination of CO, CO_2 and N in "catalysed gas" is carried out by the method of Smith *et al.* (*Anal. Chem.*, 1958, **30**, 1217) at 95° with He as carrier, in a 10-ft. W-shaped tube, containing two layers of silica gel separated by a layer of I_2O_5 (to oxidise the CO) and a layer of silver powder (to absorb the liberated iodine). The apparatus is calibrated with synthetic mixtures; the accuracy and precision are considered to be adequate for routine control. R. E. E.

702. **Determination of tar acids in black and white disinfectant fluids.** British Standards Institution (2 Park Street, London, W.1). B.S. 3265:1960. 13 pp.—Methods are described for the determination of tar acids in the two types of fluid.

703. **Estimation of adenine in gelatin with reference to restraining properties.** H. W. Wood. *J. Photogr. Sci.*, 1960, **8**, 113–118.—Gelatin (20 g) is heated under reflux for 2 hr. with 2N-$HClO_4$, cooled and filtered, and 1 ml of 5N-$AgClO_4$ is added. After standing overnight at 0° the liquid is decanted and the silver salts are centrifuged off and heated under reflux in N-HCl (10 ml) for 1 hr. The liquid is filtered and reduced on a boiling-water bath with 0·2 g of zinc dust for 15 min. Excess of zinc is removed by filtration and, after cooling to 15°, 2 ml is mixed with 1 ml of 0·1% $NaNO_2$ soln. and allowed to stand for 10 min. After removing excess of nitrite with ammonium sulphamate, 1 ml of 0·1% aq. *N*-1-naphthylethylenediamine hydrochloride soln. is added and after 30 min. the colour is read at 500 mμ. Calibration is made with soln. (0 to 0·004%) of adenine in N-HCl treated in the same way. G. H. Emmott

704. **Micro-analysis of volatile oils. III. The paper-chromatographic distribution of lower alcohols as xanthates.** R. Pohloudek-Fabini and T. Beyrich (Pharm. Inst., Ernst-Moritz-Arndt Univ. Greifswald, Germany). *Pharm. Zentralh.*, 1960, **99** (6), 341–349.—Convert the normal alcohols into the xanthates and separate them on paper buffered at pH 12 with H_2O-saturated butanol (for the C_1 to C_5 derivatives) or H_2O-saturated pentanol (for C_4 to C_7) as solvent. The xanthates may be determined by measurement of the absorption at 317 mμ of a $CHCl_3$ soln. of the nickel salts, but side-reactions prevent application of the method to quant. determination of the compounds separated by paper chromatography. A. R. Rogers

705. **Ultra-violet determination of citral in lemongrass oils which contain myrcene.** E. C. Fearns, D. A. Mitchell and B. M. Mitzner (International Flavours and Fragrances Inc., Union Beach, N. Jersey, U.S.A.). *Perfum. Essent. Oil Rec.*, 1960, **51** (7), 355–356.—West Indian lemongrass oil contains myrcene in addition to citral. Myrcene has a max. absorption at 224·5 mμ and citral at 238 mμ, and exert mutual interference. The percentage of each constituent present in an oil is calculated from the following formulae—

$$\text{citral} = (3{\cdot}46\ E^{0{\cdot}1\%}_{1\,cm} \text{ at } 238\ m\mu - E^{0{\cdot}1\%}_{1\,cm} \text{ at } 224{\cdot}5\ m\mu) \times 0{\cdot}369 \text{ and}$$

$$\text{myrcene} = (1{\cdot}47\ E^{0{\cdot}1\%}_{1\,cm} \text{ at } 224{\cdot}5\ m\mu - E^{0{\cdot}1\%}_{1\,cm} \text{ at } 238\ m\mu) \times 0{\cdot}672.$$

Determinations are carried out at concn. of ≃ 0·005 g per litre in ethanol. H. B. Heath

706. **Determination of the purity of water-soluble dyes.** J. Mýl and Z. Šolc (Dept. Phys. Chem., Inst. Chem. Technol., Pardubice, Czechoslovakia). *Chem. Průmysl*, 1960, **10** (6), 290–292.—Three methods for the determination of the purity of azo dyes of low mol. wt. (350 to 500) were compared; measurement of diffusion rates, of electrical conductivity and of the Robinson criterion (Robinson and Mills, *Proc. Roy. Soc. A*, 1931, **134**, 20), which combines the former two methods. The diffusion of dyes is less influenced by the presence of electrolyte than electrical conductivity and is therefore more suitable for the evaluation of the purity of dyes. The Robinson criterion is valid only for dyes of colloidal character. The McBain method (McBain and Lin, *J. Amer. Chem. Soc.*, 1931, **53**, 59) was used for the diffusion measurements; the dye concn. of the soln. was determined photometrically. J. Zýka

707. **Aromatic amine impurities in Yellow AB and Yellow OB food dyes.** W. D. Conway and E. J. Lethco (Nat. Cancer Inst., Nat. Inst. Health, Bethesda, Md., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 838–841.—The free amine impurities are separated from an ethereal soln. of the sample by extraction into HCl. The total aromatic amines in the extract are determined colorimetrically by a modification of the method of Bratton and Marshall (*J. Biol. Chem.*, 1939, **128**, 537). After concentration of the remaining extract, the 2-naphthylamine (**I**) is separated by partition chromatography and determined spectrophotometrically in the percolate. An alternative method for the determination of **I** involves steam-distillation of the free amine from a suspension of the dye in a saturated salt soln., extraction into ether and then into HCl, and subsequent spectrophotometric measurement in alkaline soln. The **I** content in 10 samples of two commercial samples of Yellow AB (C.I. Food Yellow 10) and Yellow OB (C.I. Food Yellow 11) ranged from 76 to 908 p.p.m. G. P. Cook

708. **Spectrophotometric determination of carboxyl in oxidised starch.** H. C. Cheung, B. Carroll and C. E. Weill (State Univ., Newark, N.J., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 818–820.—Methylene blue is used in the spectrophotometric determination of carboxyl in oxidised starches produced by the hypochlorite oxidation process. The dye binds with the carboxylate ion, influencing the absorbancy of the soln. at pH 8. The decrease of absorbancy is measured at 580 mμ, with a standard soln. of the dye for comparison. G. P. Cook

709. **Electrolytic determination of microgram quantities of water in paper.** R. G. Armstrong, K. W. Gardiner and F. W. Adams (Continental Can Co., Inc., Chicago, Ill., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 752–755.—From 10 to 200 μg of H_2O in a sample of paper as small as 0·6 mg, or $< 6\%$ of H_2O in paperboard discs ($\frac{1}{16}$ to $\frac{5}{32}$ in. diam.), can be determined in ≃ 10 min. by the procedure and instrumentation described. The H_2O is vaporised in a micro-oven and conducted in a stream of N into an electrolytic hygrometer; the electrolysis curve (mV *vs.* time) obtained is integrated electronically to record the amount of H_2O in the sample. A calibration curve is required. Except in the lower ranges the results are in fair agreement with those obtained by direct wt.-loss, but the standard deviation (10 discs) is less. Interference from NH_3 or certain organic compounds is possible. W. J. Baker

710. **Direct determination of sulphonate and non-sulphonate sulphur in spent sulphite liquor.** F. R. Foley and L. H. Johnson (Puget Sound Pulp and Timber Co., Bellingham, Wash., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 850–852.—The non-sulphonate S is oxidised to SO_4^{2-} with iodine after hydrolysis in alkaline soln., and determined gravimetrically as $BaSO_4$. The remaining compounds are wet-oxidised with HNO_3-$HClO_4$ to destroy organic matter and convert the sulphonate into SO_4^{2-}, which are determined as $BaSO_4$. The results agree well with those obtained by other methods. G. P. Cook

711. **Analysis and testing of plastics.** G. C. Ives (Yarsley Testing Lab. Ltd., Hook, Surrey, England). *Fibres & Plastics*, 1960, **21** (7), 205–208.—This is a

review of recent techniques in the analysis of rigid sheet and reinforced plastic materials. (24 references.)

712. **Spectrophotometric determination of quinol in the presence of its monomethyl ether. Application to acrylic monomers.** R. J. Lacoste, J. R. Covington and G. J. Frisone (Rohm & Haas Co., Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1960, **32** (8), 990–992.—The method is based on the blue-violet colour produced when an amine is added to quinol; the monomethyl ether (*p*-methoxyphenol) does not give a coloured reaction product. The method is applicable to acrylic monomers that contain *p*-methoxyphenol (as a polymerisation inhibitor) contaminated with traces of quinol, and 10 p.p.m. of quinol can be determined in the presence of 1000 p.p.m. of the ether with a precision of $\pm$ 5%. G. P. Cook

713. **Sorption chromatography of catechol polycondensates on polyamides.** Z. Kotásek, J. Strachota, M. Vávrová and J. Spičková (Res. Inst. Leather, Gottwaldov-Otrokovice, Czechoslovakia). *Chem. Prûmysl*, 1960, **10** (6), 321–326.—For the determination of catechol in soln. of its polycondensates the following procedure is recommended. To a glass column (internal diam. 12 mm) containing a layer (80 to 90 mm) of finely granulated polyamide (particle size 0·24 to 0·4 mm) in an aq. medium add an aq. or ethanolic soln. of the polycondensate (0·2 to 0·5 g). Elute the column with H_2O, dilute the eluate to 50 ml, and to a 5-ml aliquot add Clark-Lubbs phthalate buffer soln. (pH 3·8) (13 ml) and molybdophosphoric acid soln. (1%) (1 ml); dilute to 25 ml with H_2O and determine the extinction. The error is $\pm$ 3%. J. Zýka

714. **Colorimetric determination of ε-caprolactam.** J. Horáček, Z. Malkus and I. Schoberová (Hygiene Inst., Prague, Czechoslovakia). *Z. anal. Chem.*, 1960, **175** (6), 415–421 (in German).—The conditions for the reaction between ε-caprolactam and hydroxylamine and for the formation of the coloured Fe^{III} complex of the resulting hydroxamic acid have been studied. The following procedure is recommended. Mix 4·5M-NaOH (1 ml) and M-hydroxyammonium sulphate (1 ml), add 1 ml of neutral sample soln. (containing 0·002 to 15 mg per ml), and keep at 60° $\pm$ 1° for 4·5 hr. Cool, add 4·5M-HCl (1 ml) and 0·74M-$FeCl_3$ in 0·1M-HCl (1 ml), and make up to 10 ml. After 5 to 10 min. read the extinction of the soln. at 500 mμ against a similarly treated blank. If the soln. is too highly coloured, dilute both soln. and blank tenfold, adding sufficient $FeCl_3$ to keep the concn. 0·075M in the final soln. R. M. Rowley

715. **Determination of acetyl and sulpho-groups in acetylated and sulphonated poly(vinyl alcohol).** D. Prístavka (Dept. Anal. Chem., Inst. Chem. Technology, Bratislava, Czechoslovakia). *Chem. Zvesti*, 1960, **14** (6), 472–475.—The sample is hydrolysed with a soln. of 0·5N-NaOH in n-propanol and the acetyl groups are determined titrimetrically; sulpho-groups are determined gravimetrically as $BaSO_4$ after hydrolysis and decomposition with a mixture of Br, KI and aqua regia. J. Zýka

716. **Determination of alkaline-earth and heavy-metal ions in drier solutions.** G. Marwedel. *Farbe u. Lack*, 1960, **66** (2), 63–67.—The drier soln. (0·3 to 0·4 g) is heated with finely powdered oxalic acid (1·5 g) to 100° for $\simeq$ 10 min. The neutral oxalates formed are washed with ethanol and toluene and dried at 120° to 140°. They are then decomposed with H_2SO_4, the liberated oxalic acid is measured by titration with 0·1N-$KMnO_4$, and the metal content is calculated therefrom. The method has been used for soaps of Ca, Mg, Co, Mn, Zn, Pb and Cu. L. A. O'Neill

717. **Rapid colorimetric determination of phosphorus in high explosive compositions following a wet-ashing procedure.** R. N. Rogers (Univ. of Calif., Los Alamos, U.S.A.). *Anal. Chem.*, 1960, **32** (8), 1050.—Phosphorus has been determined in organic compounds and mixtures by a combination of liquid-fire combustion as described by Smith (*Brit. Abstr. C*, 1953, 519), and Diehl and Smith (*Anal. Abstr.*, 1960, **7**, 1396), and the molybdovanadophosphoric acid colorimetric technique. The method is safe for use with high explosive mixtures such as TNT and RDX (hexahydro-1,3,5-trinitro-sym.-triazine). The accuracy is within $\pm$ 0·01% and the standard deviation is $\pm$ 0·017% for several hundred samples containing 3% of tri-(2-chloroethyl) phosphate. G. P. Cook

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See also Abstracts—**418**, Modified Nessler reagent. **419**, Mercurated phenolphthalein and fluorescein as reagents for sulphur compounds. **500**, **644**, Determination of formaldehyde. **501**, Determination of hydrazine deriv. **524**, Sulphur in org. compounds. **611**, Determination of N. **788**, Bithionol in soap. **793**, Separation of quaternary nitrogen compounds. **821**, Polynuclear aromatic hydrocarbons in air. **823**, Cyclopentadienes in air. **854**, Gas chromatography of solid org. compounds.

4.—BIOCHEMISTRY
INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Biological fluids, animal and vegetable tissues

718. **Rapid method for moisture and fat determination in biological materials.** H. E. Wistreich, J. E. Thompson and E. Karmas (Reliable Packing Co., Chicago, Ill., U.S.A.). *Anal. Chem.*, 1960, **32** (8), 1054.—The simultaneous extraction of H_2O and fat from biological material by the use of a special flask for holding the Soxhlet extraction-thimble is described. This enables the fat to be rapidly extracted. The water is distilled over into a receiver during the extraction. G. P. Cook

719. **Determination of calcium and magnesium in rat liver.** J. R. Dunstone, N. P. Maden and H. R. Bell (Dept. of Biochem., Univ. of Queensland, Brisbane, Australia). *Analyst*, 1960, **85**, 519–521.—The method is a modification of that of Horner (*Anal. Abstr.*, 1955, **2**, 3118), in which PO_4^{3-} are removed with sodium tungstate and morpholine nitrate. The sample (3 to 5 g) is heated overnight at 700° to 800° and the ash is set aside for a time with 0·5N-HNO_3. The soln. in a centrifuge tube is mixed with 2 ml of a soln. of $Na_2WO_4.2H_2O$ (66% w/v) and 4 ml of a 28% soln. of morpholine nitrate, and after 1 hr. is centrifuged. For Ca, the supernatant liquid (1 ml) is treated with the amount of 4N-NaOH required to bring the pH to 12 [previously determined by titration with Alizarin

yellow G (C.I. Mordant Yellow 1) as indicator] in the cell of a Spekker absorptiometer, and 1 ml of a soln. containing 50 μg of Ca per ml, murexide indicator, 0·2 ml of 4N-NaOH and enough water to bring the vol. to 8 ml are added. The Ca is titrated with 0·01M-EDTA (disodium salt), and the titre is corrected for a reagent blank. For Ca and Mg, the supernatant liquid (1 ml) is diluted to 10 ml and an aliquot is titrated with 0·01M-EDTA (disodium salt) to Eriochrome black T, and corrected for a reagent blank. A correction factor of 0·97 for the vol. of the ppt. is applied. A. O. JONES

720. **Analysis of radio-isotopes in urine.** K. E. Schulte and G. Henke (Inst. f. Pharmazie u. Lebensmittelchem., Univ., Münster) *Dtsch. ApothZtg*, 1960, **100** (25), 700–706.—A review, with 78 references. A. G. COOPER

721. **Determination of strontium-90 in the skeleton.** J. Goffart (Inst. de Therapeut. Expérimentale, Univ. de Liége, Belgium). *Bull. Soc. Chim. Biol.*, 1960, **42** (2–3), 251–257.—The method depends on the conversion of ^{90}Sr into ^{90}Y. *Procedure*—Clean the bones and extract with CCl_4 to remove fat. Dry for 24 hr. at 110° then calcine for 4 hr. at 900°. Dissolve the powdered residue in 0·1N-HNO_3, neutralise to pH 1 with aq. NH_3 and extract with purified N-di-n-butyl hydrogen phosphate in butyl ether for 10 min. Centrifuge for 10 min. at 3000 r.p.m. and separate the two phases. Shake the organic phase with 10N-HNO_3, separate the aq. phase, add 10 mg of Y as carrier and precipitate as oxalate. Filter, dry with an i.r. lamp and measure the activity. Re-measure the activity after a few weeks when the ^{90}Y has decreased. The difference corresponds to the content of ^{90}Sr in the sample. There is no interference from Ca, Ba, ^{89}Sr or PO_4^{3-}. J. I. M. JONES

722. **Modification of Conway's method for estimating carbon dioxide.** H. Smith and E. A. Pask (Dept. of Anaesthetics, King's Coll., Newcastle upon Tyne, England). *Clin. Chim. Acta*, 1960, **5** (3), 446–447.—A rolled Whatman 3MM filter-paper strip (18 cm × 5 cm), previously impregnated with 10% (v/v) lactic acid soln. and warmed at 50° to remove the H_2O, is supported in a cup suspended in a 250-ml conical flask containing 5 ml of 0·1N-$Ba(OH)_2$. A Van Slyke pipette is inserted in a hole in the bung and 1 or 2 ml of plasma is transferred to the paper, the pipette being then left in position. After 1 hr. at room temp. the residual $Ba(OH)_2$ is titrated with 0·05N-HCl to pH 7·5. H. F. W. KIRKPATRICK

723. **Study of the alkaline ashing method for determination of protein-bound iodine in serum.** O. P. Foss, L. V. Hankes and D. D. Van Slyke (Med. Res. Centre, Brookhaven Nat. Lab., Upton, N.Y., U.S.A.). *Clin. Chim. Acta*, 1960, **5** (3), 301–306.—Details are given of a modified method based upon the results of an investigation of the chief factors causing erratic results. H. F. W. KIRKPATRICK

724. **Separation of salicylate metabolites by paper electrophoresis.** J. Franz, D. Schottelius, E. Arredondo, W. D. Paul and J. I. Routh (State Univ. of Iowa, Iowa City). *Proc. Iowa Acad. Sci.*, 1959, **66**, 205–209.—A method for the separation of the end-products of salicylate metabolism has been developed. A phthalate buffer of pH 3·2 and ionic strength 0·0125 to 0·0500 produced the most satisfactory separation of the metabolites. The end-products, *i.e.*, salicylic, acetylsalicylic, salicyluric and gentisic acids, could best be detected by the fluorescent spots they exhibited when the paper strips were viewed under u.v. light. The sensitivity of the method was such that 1 μg of salicylic acid could be detected as a fluorescent spot after electrophoretic separation. CHEM. ABSTR.

725. **Diagnostic composition [for the detection and estimation of glucose in urine and other fluids].** Miles Laboratories, Inc. Brit. Pat. 839,644; date appl. 14.1.57. U.S.A., date appl. 13.2.56. Addn. to Brit. Pat. 808,742, dated 17.5.56.—The test indicator comprises strips of filter-paper impregnated with a mixture of glucose oxidase 400 mg, peroxidase 2·5 mg, *o*-tolidine dihydrochloride 150 mg, potassium hydrogen phthalate 1 g, polyoxyethylene - polyoxypropylene condensate (Pluronic F–68) 1·5 g, and water 10 ml. J. M. JACOBS

726. **Determination of protein-bound carbohydrate in serum by a modified anhydrone method.** R. Shields and W. Burnett (Western Infirmary, Glasgow, Scotland). *Anal. Chem.*, 1960, **32** (7), 885–886.—The work of Tuller and Keiding (*Anal. Abstr.*, 1954, **1**, 2187), which showed that the extinction for a given concn. of carbohydrate was constant at 585 mμ despite the amount of tryptophan present, was confirmed and formed the basis of the modified method described. The extinction at this wavelength was only slightly less sensitive than that at 620 mμ and the Beer - Lambert law was obeyed. The recovery of added protein-bound carbohydrate to sera ranged from 96 to 101% over the concn. range from 100 to 200 mg per 100 ml. G. P. COOK

727. **Diagnostic composition for the [detection and] determination of albumin [in urine, etc.].** Miles Laboratories, Inc. Brit. Pat. 840,362; date appl. 23.10.58. U.S.A., date appl. 13.11.57.—The composition contains the ethyl ester of tetrabromophenolphthalein as indicator, a mixture of sodium citrate dihydrate and citric acid as buffer, and an anionic surface-active agent (2-ethylhexyl ester of sodium sulphosuccinate). J. M. JACOBS

728. **Identification of seminal stains by paper chromatography.** E. Levonen (Inst. Forensic Med., Helsinki). *J. Forensic Sci.*, 1960, **5**, 102–109.—A method for identifying seminal stains by the simultaneous detection of choline and spermine is presented. Leach a piece of the stained cloth with 1 ml of 20% trichloroacetic acid. Express the liquid from the cloth and centrifuge. Add 1 ml of water and extract the supernatant liquid with ethyl ether (2 × 2 ml). Discard the ether extract each time. Dry the residual aq. soln. on a water bath and dissolve the residue in 1 drop of 0·5N-HCl. Subject this soln. to chromatography on Whatman No. 1 paper by using an ascending solvent of isopropyl alcohol - acetic acid - water (5:1:4). Develop the chromatogram for 5 hr., dry at room temp., and spray with Dragendorff's reagent. Spermine gives a pink colour and choline a deep purple. CHEM. ABSTR.

729. **Ultra-violet spectrophotometric determination of 2-amino-2-deoxyhexoses.** J. D. Cipera (Res. Branch, Animal Res. Inst., Canada Dept. of Agric., Ottawa). *Analyst*, 1960, **85**, 517–519.—The u.v. spectrophotometric method for the determination of sugars and uronic acids by means of the reaction

with H_2SO_4 (Bath, *Ibid.*, 1958, **83**, 451) is applicable to the determination of amino-sugars, and the two most extensively occurring of these, *viz*, 2-amino-2-deoxyglucose and 2-amino-2-deoxygalactose, were used in this investigation. When applied to 1-ml portions of the aq. hexosamine soln. and 7-ml portions of 96% H_2SO_4, the use of Bath's procedure produced characteristic spectra after heating the reactants for 10 min. Both amino-sugars produced similar spectral patterns differing only in the intensity of the individual peaks. The absorption maxima were at 248 and 325 mμ, with a group of closely spaced but clearly defined peaks at 283, 289 and 298 mμ, which are not exhibited by any other class of sugars so far reported. The extinction coeff. ($E^{1\%}_{1cm}$) at these five peaks are quoted, and Beer's law is obeyed for the observed range of 6·5 to 65 μg of amino-sugar per ml of H_2SO_4. The coeff. of variation of the extinction measurements at 325 and 283 mμ did not exceed 2·62%. A study of the effect of the time of heating on the spectra showed that the group of peaks between 275 and 300 mμ behaved differently from those at 248 and 325 mμ. A. O. JONES

730. **Polarographic determination of rutin in natural extracts after chromatographic separation on polyamide powder.** J. Davídek (Zentralforschungsinst. für Lebensmittelind., Prague). *Z. Lebensmittl Untersuch.*, 1960, **112** (4), 272–275.—*Procedure*—The dry sample (2 to 20 g) is extracted with methanol in a Soxhlet apparatus for 6 hr. The solvent is evaporated, water is added, and, after filtering, the soln. is made up to 100 ml. An aliquot is added to a chromatographic column containing 2 g of polyamide powder that has been steeped in H_2O for 1 hr. The column is rinsed with H_2O under u.v. light, then eluted with methanol (30%). The brown fluorescent fraction is used for the polarographic analysis, in a Heyrovský-type V301 apparatus, with a Kalousek vessel and an external mercury sulphate electrode. The capillary has a rate of flow of 3·2 mg per sec. and a drop rate of 3·1 sec. at a reservoir height of 60 cm. To 0·2 to 1 ml of the eluate in the polarographic cell are added 5 ml of 0·2N-H_2SO_4 and 2 ml of 3M-KNO_3 while N is bubbled through the soln. After 6 min., 2 ml of 2·5M-Na acetate is added. Nitrogen is bubbled through for a further 4 min. and the polarogram is recorded. The $E_{\frac{1}{2}}$ = − 0·54 V *vs.* the S.C.E.; the reaction corresponds to a four-electron reduction of the nitroso-group.

I. DICKINSON

731. **Selective spray reagents for the identification and estimation of flavonoid compounds associated with condensed tannins.** D. G. Roux and A. E. Maihs (Leather Ind. Res. Inst., Rhodes Univ., Grahamstown, S. Africa). *J. Chromatography*, 1960, **4** (1), 65–74 (in English).—Five selective spray reagents are described which react with different groups and enable many flavonoid compounds to be identified. (*i*) A soln. of $(NH_4)_2SO_4.Fe_2(SO_4)_3$ (3%) gives blue and green colours with pyrogallol and catechol nuclei; (*ii*) ammoniacal $AgNO_3$ soln. is instantly reduced in the cold by phenolic ortho-hydroxyl groups; (*iii*) tetrazotised benzidine produces a wide range of colours with flavonoid compounds and constituent phenols; (*iv*) vanillin - toluene-*p*-sulphonic acid gives an intense violet - red colour with phloroglucinol nuclei and a weak pink colour with resorcinol nuclei; (*v*) toluene-*p*-sulphonic acid reacts with leuco-anthocyanidins not hydroxylated in the 5-position to give a scarlet colour, and with 5-hydroxylated leuco-anthocyanidins a yellow - red colour. Flavonoid compounds may be determined after two-dimensional chromatography with n-butanol - acetic acid - water (4:1:5) and 2% acetic acid by spraying with ammoniacal $AgNO_3$ soln. or tetrazotised benzidine and measuring the resulting colour in a simple densitometer.

E. C. BUTTERWORTH

732. **Paper-chromatographic determination of gibberellic acid in fermentation liquors.** M. Podojil and V. Ševčík (Mikrobiol. Abt., Biol. Inst., Tschech. Akad. Wissenschaften, Prague). *J. Chromatography*, 1960, **4** (1), 91–92 (in German).—Gibberellic acid is determined in the culture filtrates of various strains of *Fusarium moniliforme*. Aq. standard soln. (20, 60 and 120 μg per ml) and culture filtrates are adjusted to pH 2·5 to 3·0 and extracted with n-butanol. The alcoholic soln. (0·05 ml) is applied to the paper and the chromatogram is developed with butyl acetate - water. It is stained by the method of Van Overbeek *et al.* (*Plant Physiol.*, 1957, **32**, Suppl.), and the size of the test spots is compared with that of the standard spots. The maximum error is 15% and best results are obtained with gibberellic acid concn. of 40 to 100 μg per ml. E. C. BUTTERWORTH

733. **Determination of pyridoxal phosphate in the liver of normal, thyrotoxic and thyroidectomised rats.** J. Labouesse, F. Chatanger and B. Jollès-Bergeret (Fac. Sci., Paris, France). *Biochim. Biophys. Acta*, 1960, **39** (2), 374–376.—The determinations are carried out by a modification of the method of Umbreit *et al.* (*Arch. Biochem. Biophys.*, 1945, **7**, 185) with *Streptococcus faecalis*, Strain R (ATCC 8043). A 25% decrease in pyridoxal phosphate compared with normal levels is found after injection of thyroxine and a 40% increase after thyroidectomy. The reasons for the differences are discussed and a comparison is made with earlier results.

W. H. C. SHAW

734. **Micro-determination of plasma prothrombin activity using capillary blood.** E. B. Reilly, J. R. Goodman, A. Perry and B. Ward (Orange County General Hospital, Calif.). *Amer. J. Clin. Path.*, 1960, **33** (1), 92–94.—In this modification of the Owren method, 0·3 ml of capillary blood is required. (*Cf.* Ware and Stragnell, *Ibid.*, 1952, **22**, 791.)

D. E. EVANS

735. **A new spectrophotometric method for the micro-determination of [cerebroside] sulphuric acid esters in sulphatide fractions.** F. J. Witmer and J. H. Austin (Div. of Neurology, Univ. Med. Sch., Portland, Ore., U.S.A.). *Mikrochim. Acta*, 1960, (4), 502–509 (in English).—Infra-red spectrophotometry of KBr discs (300 mg of KBr) of sulphatide material at the peak at 1246 cm^{-1} (8·02 mμ), comparison with a standard, and correction for P permit determination of the content of sulphuric esters with an accuracy within ± 0·05 extinction unit. J. P. STERN

736. **Improved method of isolation and determination of cordycepin.** N. M. Kredich and A. J. Guarino (Michigan Univ., Ann Arbor, U.S.A.). *Biochim. Biophys. Acta*, 1960, **41** (2), 363–365.—An adaptation of the anthrone reaction is proposed for the assay of cordycepin (1 to 135 μg). *Procedure*—To 1 ml of sample soln., cooled in an ice

bath, add 5 ml of reagent, prepared freshly from 0·2 g of anthrone and 100 ml of 90% H_2SO_4 (150 ml of water plus 900 ml of conc. H_2SO_4). Heat at 100° for 10 min., cool, and measure the colour at 520 mμ. The calibration graph is rectilinear.

W. H. C. SHAW

737. **Technique for standardisation of methods of determination of serum bilirubin.** G. Schellong and U. Wende (Univ. Kinderklinik, Münster, Germany). *Klin. Wochschr.*, 1960, **38** (14), 703–707.—A standard soln. of bilirubin in serum (10 mg per 100 ml) is prepared by mixing 13·9 ml of fresh pooled serum with 2·0 ml of bilirubin soln. (80 mg per 100 ml), shaking, adding 0·1 ml of 4N-acetic acid, shaking well and allowing complete evolution of CO_2. A blank soln. is made by mixing similarly 13·9 ml of the same serum, 2·0 ml of 0·1M-Na_2CO_3 and 0·1 ml of 4N-acetic acid. The bilirubin soln. is prepared by placing 40 mg of bilirubin in a 50-ml flask with approx. 35 ml of 0·1M-Na_2CO_3 and mixing by rotation until clear, then making up to vol. with the Na_2CO_3 soln. The standard serum soln. is stable for many hours, and may be used for any chosen method. H. F. W. KIRKPATRICK

738. **Ion-exchange chromatographic method for separation of unesterified fatty acids in blood.** R. Biegler, E. Böhle, W. Schrade and W. Abt (I Med. Klinik, Univ. Frankfurt-a.-M., Germany). *Klin. Wochschr.*, 1960, **38** (11), 532–535.—Separation of the lipid extract of blood with the resin IR-40 (Rohm and Haas, Philadelphia, U.S.A.) is described. The method is useful for obtaining fatty acid fractions for analytical purposes and for investigating their qualitative composition.

H. F. W. KIRKPATRICK

739. **Detection of cerebrosides on paper chromatograms.** A. E. Bresler (Pennsylvania Univ. Med. Sch., Philadelphia, U.S.A.). *Biochim. Biophys. Acta*, 1960, **39** (2), 375.—Treatment of developed chromatograms with trichloroacetic acid in $CHCl_3$, followed by drying and re-spraying with an aniline oxalate reagent, gives u.v.-fluorescent spots. When chromatograms are sprayed with a soln. of Cl in $CHCl_3$, dried and treated with a benzidine - KI reagent, cerebrosides give blue spots. The tests will detect 25 μg and 10 μg of phrenosine per 2 sq. cm, respectively. W. H. C. SHAW

740. **Separation and determination of quaternary nitrogen compounds and other nitrogenous substances by ion-exchange chromatography. Application to analysis of maize extracts.** D. D. Christianson, J. S. Wall, R. J. Dimler and F. R. Senti (N. Reg. Res. Lab., Peoria, Ill., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 874–878.—Mixtures of naturally occurring quaternary nitrogen compounds (**I**) were quant. separated on Dowex 50-W resin, with HCl as the eluent, at concn. successively increasing from N to 6N. Amino-acids and certain other nitrogenous compounds were also separated by this procedure. The method was used to determine the major nitrogenous compounds in ethanol - water extracts of maize. The **I** content of the fractions was determined by spectrophotometric measurement of the periodides (Wall *et al.*, *Anal. Abstr.*, 1961, **8**, 742). Recoveries were generally > 93%. G. P. COOK

741. **Elson-Morgan reaction of *N*-substituted isoglucosamines.** Toshio Ohnishi and Yoshiyuki Inoue (Coll. of Agric., Univ., Sakyo-ku, Kyoto). *J. Agric. Chem. Soc. Japan.*, 1959, **33** (1), 31–34.—The Elson-Morgan reaction (*Biochem. J.*, 1933, **27**, 1824) of *N*-substituted isoglucosamines exhibits an absorption at 530 mμ, as is shown by the same reaction by hexosamines, accompanying an absorption at 560 to 570 mμ. *N*-Arylglucosylamines give no coloration, but other *N*-substituted glucosylamines show a faint coloration. The reaction mechanism of the coloration is discussed.

S. NATORI

742. **Spectrophotometric determination of betaines and other quaternary nitrogen compounds as their periodides.** J. S. Wall, D. D. Christianson, R. J. Dimler and F. R. Senti (N. Reg. Res. Lab., Peoria, Ill., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 870–874.—The method of Appleton *et al.* for the determination of choline (*J. Biol. Chem.*, 1953, **205**, 803) was modified to permit the analysis of further compounds, and is based on isolation of their periodides, dissolving these in dichloroethane and measuring the extinctions at 365 mμ. The calibration curves are essentially linear and reproducible with a precision of ± 2 μg in the range from 10 to 50 μg of a quaternary nitrogen compound. The procedure was developed for the detection and determination of betaines and other quaternary compounds in the effluent from chromatographic columns employed for their separation from mixtures.

G. P. COOK

743. **Simple analysis for normetanephrine (3-methoxynoradrenaline) and metanephrine (3-methoxyadrenaline) in urine.** J. J. Pisano (Lab. of Clin. Biochem., Nat. Heart Inst., Bethesda, Ind., U.S.A.). *Clin. Chim. Acta*, 1960, **5** (3), 406–414.—These compounds are separated and determined, after acid hydrolysis of the urine, by adsorption on Amberlite CG-50 resin, elution, conversion into vanillin by oxidation with periodate and spectrophotometric measurements at 350 and 360 mμ.

H. F. W. KIRKPATRICK

744. **Separation and determination of metaadrenaline [3-methoxyadrenaline] and metanoradrenaline [3-methoxynoradrenaline] by high-voltage paper electrophoresis.** W. von Studnitz (Dept. of Clin. Chem., Gen. Hosp., Malmö, Sweden). *Clin. Chim. Acta*, 1960, **5** (3), 447–448 (in English).—A tri(hydroxymethyl)methylamine buffer of pH 8·4 and Whatman 3MM filter-paper are used. A potential gradient of 45 V per cm is applied for 2 hr., the paper is dried for 40 min. at 80° then sprayed with diazo reagent (*p*-nitroaniline) and dried in a current of air. The violet spots are cut out, the colour is eluted with alkaline methanol and measured at 520 mμ. Under these conditions, meta-adrenaline and metanoradrenaline migrate 7·5 cm and 5·0 cm, respectively, towards the cathode. The method is applicable to urine hydrolysed at pH 1 and extracted with ethyl acetate at pH 9. H. F. W. KIRKPATRICK

745. **Paper chromatography of some guanidine derivatives.** R. Pant and S. S. Dubey (Allahabad Univ., India). *Biochim. Biophys. Acta*, 1960, **41** (3), 536–538.—Five solvent-systems for the one- and two-dimensional chromatography of 7 guanidine derivatives on Whatman No. 1 paper are given and R_F values are tabulated. The compounds are detected by the Sakaguchi reaction and creatine with a diacetyl - 1-naphthol reagent.

W. H. C. SHAW

746. **A modified two-dimensional paper-chromatographic system for the separation of dinitrophenylamino-acids.** F. W. Pairent and M. B. Williamson (Dept. of Biochem., Graduate School and Stritch School of Medicine, Loyola Univ., Chicago, Ill., U.S.A.). *J. Chromatography*, 1960, **4** (1), 80–82 (in English).—Chromatography is carried out on Whatman No. 1 paper (22 in. × 18 in.) impregnated with 0·05M-phthalate buffer (pH 6·0). After application of the sample soln. and equilibration in an atmosphere of n-pentanol and water for 2 hr. the chromatogram is developed by the descending technique for 15 to 18 hr., with n-pentanol saturated with the buffer. The paper is air-dried in the dark for 3 to 6 hr. and then developed similarly in the second direction for 15 to 18 hr. with 1·5M-Na_2SO_4 - 0·05M-phthalate buffer (pH 6·0). R_F values for 19 dinitrophenylamino-acids in both solvents relative to 2,4-dinitrophenol are listed.

E. C. Butterworth

747. **Indirect polarographic determination of amino-acids by the copper phosphate method.** W. J. Blaedel and J. W. Todd (Chem. Dept., Univ. Wisconsin, Madison, U.S.A.). *Anal. Chem.*, 1960, **32** (8), 1018–1021.—The α-amino-acid is converted into the 1:2 copper chelate with copper phosphate. The 1:1 copper - EDTA complex is then formed, and measured polarographically at an $E_{\frac{1}{2}}$ of $\simeq -0{\cdot}4$ V *vs.* the S.C.E. The diffusion current is proportional to the amino-acid concn. and is compared with that produced by a standard copper - EDTA soln. The error of the method is $< 4\%$ at a concn. of 10^{-3}M, and the limit of detection is 2×10^{-4}M.

G. P. Cook

748. **Infra-red spectra of amino-acids and related substances in water.** F. S. Parker and D. M. Kirschenbaum (Dept. of Biochem., State Univ., New York, Brooklyn, U.S.A.). *Nature*, 1960, **187**, 386–388.—Some results are reported of a systematic investigation of the i.r. spectra of various small molecules of biological importance. For the examination of aq. soln., i.r. cells with barium fluoride windows have been used.

K. A. Proctor

749. **Improved microbiological assay for *N*-formimidoylglutamic acid.** R. E. Davis and P. Onesti (Dept. of Haematology, Royal Perth Hospital, W. Australia). *Aust. J. Exp. Biol. Med. Sci.*, 1960, **38** (3), 239–244.—*N*-Formimidoylglutamic acid in urine is indicative of folic acid deficiency. It is determined in urine by conversion into glutamic acid by heating after removal of endogenous glutamic acid and glutamine. The organism used is a specially prepared culture of *Lactobacillus arabinosus* 17–5 (ATCC 8014). The growth is measured turbidimetrically against standards. Tests with known amounts of Ba *N*-formimidoylglutamate gave a mean recovery of 66% of the theoretical amount of glutamic acid over a range of 0·025 to 0·15 μmole per ml. J. I. M. Jones

750. **Applications of nitrometry. XIX. Determination of proline in proteins.** M. Yokoo (Res. Lab., Takeda Pharm. Ind. Ltd., Juso-Nishini-cho, Higashiyodogawa-ku, Osaka, Japan). *Chem. Pharm. Bull., Japan*, 1960, **8** (7), 571–574 (in English).—Alone among amino-acids from proteins, proline has a secondary amino-group that can be nitrosated and then reduced to an *N*-amino-group which, on oxidation with $Fe(CN)_6^{3-}$ yields N (measured with a nitrometer). A preliminary experiment shows that alkaline hydrolysis with 5N-NaOH at 100° to liberate the proline requires 6 hr. for egg albumin, 22 hr. for casein and 14 hr. for protamine sulphate. *Procedure*—A sample of protein containing 0·03 to 0·07 millimole of proline is hydrolysed with 2 ml of 5N-NaOH and, after cooling, is treated with 2 ml of glacial acetic acid and 1 ml of 60% aq. KNO_2 for 30 min. at 30°. Excess of HNO_2 is decomposed with 0·5 g of sulphamic acid. The soln. is then reduced with 1 g of zinc dust and 1·5 ml of conc. HCl, shaken for 15 min. with a further 15 ml of HCl and then kept with occasional shaking for 30 min. in the presence of 0·5 g of Devarda's alloy. After filtering and making the filtrate up to 25 ml, a 2-ml portion is oxidised with $K_3Fe(CN)_6$ and the N evolved is measured (115 μg of protein ≡ 11·2 cu. mm of N at s.t.p.). Results for the proline content of various proteins and recovery experiments with added proline are reported. E. J. H. Birch

751. **Detection of hydroxylysine in serum protein.** E. Waldschmidt-Leitz, G. Bretzel and L. Keller (Inst. für Org. Chem., Tech. Hochsch., München, W. Germany). *Naturwissenschaften*, 1960, **47** (11), 254.—The detection and measurement of hydroxylysine in α- and γ-globulin have been made. Two-dimensional paper chromatography of samples from human and rabbit serum, with n-butanol - formic acid - water or phenol - water, gives R_F values of 0·045 and 0·204, respectively, the quantitative measurement being made with the automatic instrument of Hannig (*cf. Clin. Chim. Acta*, 1959, **4**, 51). E. G. Cummins

752. **3-Hydroxykynurenine in human urine.** S. L. Tompsett (Northern Gen. Hosp., Edinburgh, Scotland). *Clin. Chim. Acta*, 1960, **5** (3), 415–419.—This substance is separated from urine by means of the ion-exchange resin Dowex 50-X12, and determined by a molybdate - phosphate reaction. H. F. W. Kirkpatrick

753. **Quantitative micro-determination of histamine in tissue extracts.** N. Matussek (Dtsch. Forschungsanst. f. Psychiatrie, Max-Planck-Inst., München). *Naturwissenschaften*, 1960, **47** (14), 324.—The extracts are submitted to high-voltage electrophoresis, and the histamine bands are then eluted and tested on isolated guinea-pig ilium. Pyridine acetate buffer (pyridine - glacial acetic acid - water (10:1:89)) (pH 6·0) is used, and electrophoresis is carried out for 60 min. at 40 V per cm on S. & S. paper 2043b. As a control, known quantities of histamine are applied at a distance of 2 to 3 cm from the sample, the amount used depending on the approx. content of the sample. After electrophoresis and removal of the buffer, the outside strips are cut off and treated with ninhydrin. At the point where the histamine is found (15 to 16 cm towards the cathode), squares of the paper (2 cm × 2 cm) are cut out, disintegrated and shaken well in 1 ml of Tyrode soln. The supernatant liquid is used for the assay. The time required is < 2 hr., and 0·04 to 0·06 μg of histamine can be determined. B. Heining

754. **Polarographic determination of cystine and cysteine in wool.** L. Beníšek (Wool Res. Inst., Brno, Czechoslovakia). *Z. anal. Chem.*, 1960, **175** (4), 244–255 (in German).—Cystine (**I**) and cysteine (**II**) in wool hydrolysates prepared with H_2SO_4 are determined polarographically (dropping mercury electrode); the cathodic wave is used for **I** ($E_{\frac{1}{2}} = -0{\cdot}37$

V) and the anodic wave for **II** ($E_{\frac{1}{2}} = -0{\cdot}05$ V). No further chemical treatment is required. Oxygen interferes in the determination of **I** and Cl^- in that of **II**. An additional wave observed is due to SO_2, probably derived from sulphonic or sulphinic acids in the wool; it increases with increasing damage to the fibre. The accuracy on 15 to 30 mg of **I** is within ± 0·1 mg, but recovery of **II** (3 mg) is about 4% low. The reproducibility is satisfactory. *Procedure*—Extract the sample (250 mg) with ethyl ether, dry at 105° for 1 to 2 hr., re-weigh, and hydrolyse with 30% H_2SO_4 (5 ml) at 105° for 8 hr. Dilute the soln. to 25 ml and filter. Polarograph 2 ml under N between 0 and 0·8 V; then add 2 ml to a 0·005M soln. (1 ml) of **I** and measure the increase in the height of the wave. Similarly use a 5-ml sample, 2 ml of 0·005M-**II** and the range 0 to 0·4 V for determining **II**. J. P. STERN

755. **Determination of exchangeable taurine in the organs of the rat.** Huynh Vinh An and P. Fromageot (Centre d'Études Nucléares de Saclay, Gif-sur-Yvette, Seine et Oise, France). *Bull. Soc. Chim. Biol.*, 1960, **42** (2–3), 221–226.—Observations by a number of workers indicate that taurine, hitherto considered to be an end-product of metabolism of sulphur-containing amino-acids, possesses a metabolism of its own. A detailed study has been made of the taurine content of the organs of the rat, measuring the tissue-exchangeable amounts by diluting taurine ^{35}S *in vitro* with intracellular taurine. The activity is measured after conversion of the taurine into dinitrophenyltaurine (DNP-taurine) with fluorodinitrobenzene, separating the DNP-taurine chromatographically from dinitrophenol, dinitroaniline and DNP-phosphoethanolamine. *Procedure*—The homologous organs (0·5 to 1 g) of at least 5 rats of the same sex were ground in a Servall or Potter-Elvejhem apparatus with 2 ml of H_2O per g of fresh tissue and the extractable taurine was determined by Awapara's method (*J. Biol. Chem.*, 1956, **218**, 571). To a second portion of the mixed organs an accurately measured amount of ^{35}S-taurine was added in amount approx. equal to the taurine found in the first portion. After homogenisation at 0°, the taurine was separated from amino-acids by passage through a column of Dowex 50, the filtrate being then passed through an Amberlite-IRA column, from which the adsorbed taurine was eluted with N-acetic acid before conversion into DNP-taurine. The amounts of exchangeable taurine found in the various organs, including heart, lungs, liver, brain, muscle, bone marrow and various glands, were equal to the amounts of total extractable taurine.
J. I. M. JONES

756. **Kjeldahl determination of nitrogen [in proteins].** F. G. Sietz. *ChemikerZtg*, 1960, **84** (11), 362–364.—Mixtures of $CuSO_4$ and Se are not generally suitable as catalysts for the Kjeldahl determination of N in proteins. Low results may be obtained, especially with cystine, methionine and tryptophan. A. R. ROGERS

757. **Determination of sulphydryl [mercapto] groups in reduced hair keratin.** H. H. Stein and J. Guarnaccio (The Toni Co., Chicago, Ill., U.S.A.). *Anal. Chim. Acta*, 1960, **23** (1), 89–97.—Traces of thioglycollate, used to reduce the disulphide bonds in the keratin, are extracted during 2 hr. with glacial acetic acid in a micro Soxhlet apparatus. The sample is washed with isopropyl alcohol before and after extraction and is finally dried at 110° *in vacuo* and cooled in N. *Procedure*—To 20 mg of prepared sample add ≃ 10 mg of iodoacetic acid and 10 ml of borate - KNO_3 buffer soln. (pH 10). After 45 min. with occasional stirring, take a 5-ml aliquot, add 6N-HNO_3 to reduce the pH to 7 and $NaHCO_3$ until no more CO_2 is evolved. Titrate the I^- potentiometrically with 0·001N-$AgNO_3$, with the use of a silver electrode, a S.C.E. and a M-NH_4NO_3 - 4% agar bridge. H. N. S.

758. **Rapid staining of serum lipoprotein electropherograms.** R. L. Searcy, L. M. Berquist and R. C. Jung (Los Angeles County Osteopathic Hosp., Calif., U.S.A.). *Clin. Chim. Acta*, 1960, **5** (3), 449–450.—Marker strips for the location of the α- and β-lipoprotein areas are dried in air and sprayed lightly with a 10% soln. of molybdophosphoric acid in abs. ethanol. The strips are allowed to dry for about 30 sec. in an oven at 130° to 140°; sharp blue - green staining of the lipoprotein areas takes place. The colour is retained indefinitely when exposed to air and light.
H. F. W. KIRKPATRICK

759. **Automatic extraction of urinary phenolic steroids.** C. Dumazert and J. B. Mazet (Lab. de Chim. Fac. de Méd. et de Pharm., Marseille, France). *Bull. Soc. Chim. Biol.*, 1960, **42** (2–3), 275–277.—The apparatus described, which can be made completely automatic, is recommended for the ether extraction of phenolic steroids before their determination by the method of Jayle *et al.* (*cf. Anal. Abstr.*, 1959, **6**, 4109). J. I. M. JONES

760. **Thin-layer chromatography of weakly polar steroids.** M. J. D. van Dam, G. J. de Kleuver and J. G. de Heus (D. S. van Schuppen N.V., Veenendaal, The Netherlands). *J. Chromatography*, 1960, **4** (1), 26–33 (in English).—Smooth glass plates (5 cm × 20 cm and 20 cm × 20 cm, and 0·37 cm thick) coated with a thin layer of Silica Gel G (Merck) are used to separate weakly polar steroids, and the technique of using these chromatostrips and chromatoplates is described. The spray reagent is a saturated soln. of $SbCl_3$ in $CHCl_3$, and R_F values are tabulated for 17 steroids with 13 solvent systems. The method gives rapid and good separations.
E. C. BUTTERWORTH

761. **Rapid determination of total and free cholesterol in serum.** P. V. Ferro and A. B. Ham (Dept. of Chem., Dade Reagents Inc., Miami, Florida). *Amer. J. Clin. Path.*, 1960, **33** (6), 545–549.—In this colorimetric method, an acetic acid - H_2SO_4 colour-development reagent is used, either directly, or with an isopropyl alcohol extract of serum that has been saponified and pptd. with digitonin. The direct method, which can be used only for the estimation of total cholesterol, gives average values 15% higher than those obtained after saponification, owing to the presence of non-sterol components; a high bilirubin concn. is an indication for saponification, but protein concn. of up to 30% show negligible interference. Of 200 samples, 82·5% gave values within the range 151 to 270 mg per 100 ml. The maximum difference between any two values in ten tests of a single sample was 3%. D. E. EVANS

762. **Micro-determination of free and esterified cholesterol in cerebrospinal fluid.** N. M. Papadopoulos, W. Cevallos and W. C. Hess (George Univ.,

Washington, D.C.). *J. Neurochem.*, 1959, **4**, 223–228.—A micro-procedure for the extraction, chromatographic separation on a silicic acid column, and colorimetric determination by $FeCl_3$ - H_2SO_4 reagent, of free and esterified cholesterol in cerebrospinal fluid is described. The two fractions of cholesterol in cerebrospinal fluid were identified by paper chromatography, and their R_F values determined.
CHEM. ABSTR.

763. **Micro-analytical separation of steroids by gas chromatography.** C. C. Sweeley and E. C. Horning (Lab. of Chemistry of Natural Products, Nat. Heart Inst., Bethesda, Md., U.S.A.). *Nature*, 1960, **187**, 144–145.—A polar-phase system is described suitable for the separation of some steroids. The column packing was prepared by a soln. technique (*cf.* Horning *et al.*, *Chem & Ind.*, 1959, 751) with a 10% $CHCl_3$ soln. of ethanediol - isophthalic acid polyester and 60 to 80-mesh acid-washed Celite 545. The coated 'Celite' (20% stationary phase) was vibration-packed in a glass U-column (100 cm × 2 mm) and conditioned briefly at 200°. Thermal stability of the column was good. Cholesterol methyl ether and cholestanol methyl ether could not be separated, but androstane-3,17-dione, androst-4-ene-3,17-dione and cholestanone had different retention times. Hydroxyl-substituted compounds were not fully investigated. The method can be used for the separation of fatty acid esters, but is not quantitative. R. A. HENDEY

764. **Polarographic determination of pregnane-3α,17α,20α-triol and other acetaldehydogenic urine steroids.** L. Stárka and H. Brabencová (Res. Inst. for Endocrinol., Prague, Czechoslovakia). *Clin. Chim. Acta*, 1960, **5** (3), 423–430 (in German).—The urine is extracted and the extract is hydrolysed with glycuronidase as described by Stern (*J. Endocrin.*, 1957, **16**, 180). Acetaldehyde and formaldehyde can be determined on the same polarogram after periodate oxidation, the excess of periodate being removed with bisulphite soln. The results by this method showed good correlation with those by the method of Stern. H. F. W. KIRKPATRICK

765. **Estimation of pregnanetriol and 17-hydroxypregnanolone in urine in congenital adrenal hyperplasia.** M. Bell and H. Varley (Royal Infirmary, Manchester, England). *Clin. Chim. Acta*, 1960, **5** (3), 396–405.—The method of Stern (*J. Endocrin.*, 1957, **16**, 180) is investigated and extended. Treatment with borohydride converts 17-hydroxypregnanolone (3α,17α-dihydroxy-5β-pregnan-20-one) into the corresponding pregnanetriol (**I**) and the determination of **I** before and after treatment gives a measure of both steroids. Details of the method and results are given.
H. F. W. KIRKPATRICK

766. **Enhancement of the fluorescence of progesterone (and other steroids) in sulphuric acid.** J. C. Touchstone and T. Murawec (Sch. of Med., Univ. of Pennsylvania, Philadelphia, U.S.A.). *Anal. Chem.*, 1960, **32** (7), 822–824.—Certain steroids, when heated with 2N-methanolic KOH at 60° for 30 min. before being dissolved in H_2SO_4, show greater fluorescence intensity than when dissolved in H_2SO_4 alone. This treatment causes a hundred-fold increase in the fluorescence of progesterone, and steroid concn. of 0·01 to 1 μg per ml of H_2SO_4 can be satisfactorily measured. Oestrogens show decreased fluorescence with this treatment. G. P. COOK

767. **Aldosterone separation from biological extracts by two reversed-phase paper-chromatographic systems.** J. Di Perri, G. Ravenni and M. Rubegni (Inst. of Med. Semiology, Univ. of Siena, Italy). *Clin. Chim. Acta*, 1960, **5** (3), 420–422 (in English).—Two successive one-dimensional descending chromatographic separations are made with the following systems, *viz*, toluene - n-octanol - methanol - H_2O (49:1:25:25) and toluene - light petroleum (boiling-range 40° to 70°) - methanol - H_2O (5:5:7:3). The paper strips are saturated with the toluene phase and the chromatograms are developed with the methanol - H_2O phase as mobile solvent for 5 to 6 hr. The steroid is detected in u.v. light and eluted with ethanol. H. F. W. KIRKPATRICK

768. **Demonstration of carbohydrase activity in commercial papain by paper chromatography.** E. Zoch (Physiol.-chem. Inst., Univ. des Saarlandes in Homburg/Saar, Germany). *J. Chromatography*, 1960, **4** (1), 21–25 (in German).—Papain powder (5 g) suspended in water (50 ml) is centrifuged for 10 min. at 4000 r.p.m. and the aq. extract is treated with an equal vol. of acetone at 3°. The ppt. is separated by centrifugation and dried *in vacuo* at −4°, and to 0·5 g of the dried preparation is added 5 ml of phosphate buffer (pH 6·8) or acetate buffer (pH 5·0). After centrifuging, 0·5 ml of the clear soln. is incubated at 37° for 24 hr. with an equal vol. of various substrates (5% aq. soln. of poly-, tri- and di-saccharides). The incubated soln. and also non-incubated mixtures are chromatographed with the ascending technique and n-butanol - acetic acid - water (4:1:5) as the solvent system. From the monosaccharides identified it is concluded that a dried acetone preparation of commercial papain contains amylase, two α-glucosidases, a β-glucosidase, an α-galactosidase, a β-galactosidase and an invertase. E. C. BUTTERWORTH

769. **Interference of biochemically important reducing agents with the diazotisation of sulphanilamide [in the determination of nitrate reductase].** H. R. Schreiner and A. P. Rinfret (Linde Co., Union Carbide Corp., Tonawanda, N.Y., U.S.A.). *Biochim. Biophys. Acta*, 1960, **39** (2), 343–345.—A study is made of the interference by reduced di- and tri-phosphopyridine nucleotides and of cysteine on the colorimetric determination of nitrite (nitrate-reductase activity) with sulphanilamide and *N*-1-naphthylethylenediamine. The mechanisms of the reactions are discussed. W. H. C. SHAW

770. **pH-static method for the assay of arginase.** M. Rigbi (Hebrew Univ., Jerusalem, Israel). *Bull. Res. Council Israel, A*, 1960, **9** (1–2), 149–156.—The δ-amino-group of ornithine is less basic than the guanido-group of arginine, and urea is an extremely weak base, so that arginase activity is accompanied by the release of H^+. By measuring the rate of addition of alkali to a weakly buffered arginase system, containing a large amount of substrate, the arginase content can be determined. Alternatively, the method may be used for the determination of L-arginine by measuring the amount of alkali required to complete the hydrolysis. Potentiometric titration curves and consideration of the activity of the enzyme indicate that the sensitivity of the method is greatest near pH 10. A "pH 10·2 arginase unit" is defined as the amount of enzyme that will decompose 1 μmole of arginine in 1 min. at 25° and pH 10·2 at a substrate concn. of 0·285M.

At this pH and temp., 1 μmole of alkali added is equivalent to 2·5 μmoles of L-arginine hydrolysed. G. P. COOK

See also Abstracts—**419**, Mercurated phenolphthalein and fluorescein as reagents for sulphur compounds. **436**, Oxygen in body fluids. **448**, Determination of K. **786**, Phenothiazine deriv. in biological materials. **789**, Hypoglycaemic sulphamides in blood and urine. **798**, Separation of milk proteins. **863**, Electrophoresis of amino-acids.

Pharmaceutical analysis

771. **Simple micro-method for the quantitative determination of the percentage content of aqueous solutions [of drugs].** R. Fischer, E. Pinter and H. Auer (Pharmakognost. Inst., Univ., Graz, Austria). *Pharm. Zentralh.*, 1960, **99** (6), 299–312.—Heat the sample in contact with a test liquid in a capillary tube on a Kofler hot-stage and note the temperature at which the meniscus disappears (*cf.* Fischer and Horner, *Mikrochim. Acta*, 1953, 386). Critical mixing temperatures are tabulated as a function of concn. of aq. soln. for 60 samples of alcohols, carboxylic acids, salts, phenols and local anaesthetics; 17 different test liquids were used. Only 1 to 3 mg of sample is needed and the time of determination is 15 min. With some samples the accuracy is 0·05% absolute and it is always better than 0·5%. A. R. ROGERS

772. **Determination of morphine in opium.** C. Rösler, S. Pfeifer and F. Weiss (Pharm. Inst., Humboldt Univ., Berlin). *Pharm. Zentralh.*, 1960, **99** (6), 349–359.—Various methods for the determination of morphine in opium and its preparations are compared. A modified lime method in which all sources of error are allowed for, or a method which involves isolation of morphine as the dinitrophenyl ether, is recommended for inclusion in the D. A. B. VII. A. R. ROGERS

773. **The determination of pharmaceutically important organic nitrogenous bases by titration of their picrates in acetic acid. II. Determination of quinine in some pharmaceutical preparations.** M. Hädicke and K. Howorka (Staat. Inst. für Arzneimittelprüfung, Jena, Germany). *Pharm. Zentralh.*, 1960, **99** (6), 312–317.—The method described previously (*cf.* Howorka and Hädicke, *Anal. Abstr.*, 1960, **7**, 2954) has been successfully applied to the determination of quinine alone in Metapyrin-Chinin or in the presence of calcium gluconate, ascorbic acid and acetylsalicylic acid, and leptazol. A. R. ROGERS

774. **Polarographic determination of acetophenone in injection solutions of lobeline hydrochloride.** L. Miczko (Vojenský Útvar 9965, Bystřice Pod Hostýnem, Czechoslovakia). *Českosl. Farm.*, 1960, **9** (6), 314–315.—In Britton and Robinson buffer soln. of pH 6·0 to 6·8 the polarographic waves of acetophenone and lobeline can be distinguished; acetophenone is reduced at a more negative potential. *Procedure for injections*—Dilute 1 ml of the sample (containing 1% of lobeline) to 100 ml with buffer soln. of pH 6·50 and transfer 10 ml to a polarographic cell. Remove O by bubbling with N for 3 min. and register the polarographic wave. The method is suitable for the determination of 0·5 to 0·8% of acetophenone in lobeline hydrochloride soln. J. ZÝKA

775. **Potentiometric determination of sodium chloride and theophylline in a mixture in the presence of hydroxyethyltheophylline.** C. Peciar and K. Linek (Chem. Inst. Acad. Sci., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1960, **14** (6), 425–433.—The potentiometric argentimetric method is based on the fact that the silver salt of theophylline (**I**) is soluble in a medium of pH 2 and does not interfere in the determination of NaCl; after changing the pH to 9 to 10, **I** can be determined. Hydroxyethyltheophylline does not interfere. *Procedure*—Dissolve the sample (containing 10 to 100 mg of **I**) by heating to 50° to 70° in H_2O (20 ml), cool, add N-H_2SO_4 (2 ml) and titrate Cl^- potentiometrically with 0·1N-$AgNO_3$. Then add 2N-Na_2CO_3 (4 ml) and titrate **I**. J. ZÝKA

776. **The chemical evaluation of digitalis drugs (*D. purpurea* and *D. lanata*). III.** W. Hauser and W. Berger (Pharmakog. Inst., Univ., Graz, Austria). *Sci. Pharm.*, 1960, **28** (2), 161–166.—Extract an aq. macerate of the drug with $CHCl_3$ and apply it to a column of alumina previously treated with a 2·5% soln. of formic acid in ethanol-free $CHCl_3$. Elute digitoxin and gitaloxin with a 4% soln. of ethanol in $CHCl_3$ and gitoxin with a 40% soln. of ethanol in $CHCl_3$ and determine by the method of Kedde (*Pharm. Weekbl.*, 1947, **82**, 741). Alternatively, elute all of the digitoxin and gitaloxin and about one-fifth of the gitoxin with a 4·5% soln. of ethanol in $CHCl_3$, determine by the Kedde method and calculate as digitoxin; the percentage found multiplied by 100 is called the "value number" ("Wert-Zahl") and is thought to be a measure of the potency of the sample. A. R. ROGERS

777. **Studies on a new plate test with *Escherichia coli* for the simplified and improved microbiological determination of penicillin in pharmaceutical preparations and fermentation samples.** W. Oberzill (Biochemie-G.m.b.H., Kundl/Tirol, Austria), *Sci. Pharm.*, 1960, **28** (2), 102–123.—Details are given of a method for the cup-plate assay of benzylpenicillin and phenoxymethylpenicillin at concn. in the range 1000 to 5000 units per ml with *E. coli* B as test organism. No prior dilution is necessary. A. R. ROGERS

778. **Chemical determination of streptomycin and penicillin in mixed preparations.** G. Machek (Biochemie-G.m.b.H., Kundl/Tirol, Austria). *Sci. Pharm.*, 1960, **28** (2), 97–101.—Mix the sample (containing ≃ 0·5 g of streptomycin or dihydrostreptomycin and 0·2 to 1 g of procaine penicillin as well as buffer substances) with H_2O (15 ml) and butyl acetate (20 ml), adjust to pH 2·1 by addition of 2N-HCl and shake for 5 min. Extract a 1-ml aliquot of the filtered upper layer with phosphate buffer soln. (pH 7·2) (10 ml) and determine the penicillin in the extract iodimetrically or microbiologically. Mix the filtered lower layer with butyl acetate (20 ml), adjust to pH 9·5 by addition of 2N-NaOH, add M-$BaCl_2$ (2 ml) and shake for 1 min.; centrifuge, separate and dilute the aq. phase to 50 ml, adjust the pH of a 20-ml aliquot to 5·8 by addition of 2N-HCl and titrate the streptomycin or dihydrostreptomycin potentiometrically with 0·1N-NaOH to pH 9·6. A. R. ROGERS

779. **Photometric determination of tetracyclines on the basis of complex formation with ammonium molybdate.** L. Mázor and M. Pápay (Inst. f. Allg. Chem., Tech. Univ., Budapest, Hungary). *Z. anal. Chem.*, 1960, **175** (5), 355–359.—The blue complex formed between the tetracyclines (0·001M in HCl,

pH 1·0) and ammonium molybdate (0·1M aq.) in the presence of 50% (v/v) ethanol has been used for determinations in the range 0·025 to 0·5 mg per ml in fermentation broths, after pptn. of Ca as oxalate.
E. G. CUMMINS

780. **The chromatography of tetracycline antibiotics. I. Qualitative separation.** G. Coppi (Carlo Erba Inst. of Therap. Res., Milan, Italy). *Farmaco, Ed. Prat.*, 1960, **15** (7), 407–410.—Separation of antibiotics of the tetracycline group from each other and from their epimers and anhydro-derivatives is effected on Whatman 3MM paper (18 cm × 45 cm) impregnated with pH 3·5 buffer and freed from excess of liquid by pressing between sheets of filter-paper. To the damp paper apply 2-μl spots (⊃ 6 to 8 mm in diam.) of the soln. to be tested. Not more than 15 to 20 min. should elapse between impregnating with buffer and developing the spots. Develop the chromatogram by the descending technique at 25° for about 4 hr. with nitroethane - benzene - collidine (100:50:24·5) or nitroethane - benzene - pyridine (20:10:3), then dry, expose to conc. ammonia vapour for a few minutes, then examine by u.v. light. Tetracycline, oxy-, chlor-, demethyl-, epi- and epichlor-tetra-cyclines give yellow fluorescent spots with R_F values 0·21, 0·14, 0·46, 0·33, 0·07 and 0·08, respectively. Anhydro-derivatives of tetracycline, epi- and chlor-tetracycline give orange fluorescent spots with R_F values of 0·74, 0·43 and 0·80, respectively. Chemically degraded tetracyclines give blue fluorescent spots. Nitromethane, toluene, aniline or piperidine may be used instead of nitroethane, benzene, collidine or pyridine, respectively.

II. Quantitative separation. G. Coppi. *Ibid.*, 1960, **15** (7), 411–418.—The quantitative analysis of commercial tetracycline and chlortetracycline, which usually contain both antibiotics, their epimers and their anhydro-derivatives, is described. *Procedure*—Along a line 8 cm from the edge of a sheet of Whatman 3MM paper impregnated with McIlvaine's phosphate buffer (pH 3·5) distribute 300 to 600 μg of sample along a length of 10 cm. Develop, etc., as described above, with nitro-ethane - benzene - collidine (100:50:24·5). Cut out the spots, reduce to small pieces and shake in a stoppered tube with 20 ml of 0·1N-HCl till the paper is completely disintegrated. The tetra-cycline spot should include the short tail arising from epimerisation during development. Filter through Whatman No. 4 filter-paper. Add 1 ml of 6N-HCl to 5 ml of filtrate in a 10-ml graduated tube and place in a boiling-water bath for 5 min. Cool and restore the vol. to 6 ml with H_2O. This treatment converts all these antibiotics into their intensely yellow anhydro-derivatives. Measure the extinction at 457 mμ. Carry out a blank test in the same way omitting the heating. The difference in the readings is referred to a standard curve prepared from pure materials by the same method. Different standard curves are prepared for the different constituents (spots), *viz*, tetracycline, chlor- and epi-tetracycline hydrochlorides. Recovery experiments with pure samples of these products gave recoveries of 93 ± 3, 70 ± 3, and 99 ± 2%, respectively, and the amounts obtained in an analysis are to be corrected on this basis. Anhydro-tetracyclines in the samples cannot be determined after chromatographic development, but can be calculated from the readings on an untreated solution. The solvent mixture used for development is that which results in minimum epimerisation.
J. I. M. JONES

781. **The determination of chlortetracycline in animal tissues.** J. Hess and J. Čapková (Výzkumný Ústav Antibiotik, Prague, Czechoslovakia). *Průmysl Potravin*, 1960, **11** (6), 331–333.—Chlor-tetracycline (**I**) is determined by a cylinder-plate method after extraction of the tissue with acetone - 4N-HCl - water (13:1:6). The organism used is *Bacillus cereus* var. *mycoides* ATCC 9634. The sensitivity of the method is 0·04 μg of **I** per g of animal tissue.
P. GLOVER

782. **Insulin in blood.** P. J. Randle and K. W. Taylor (Dept. of Biochem., Univ. of Cambridge, England). *Brit. Med. Bull.*, 1960, **16** (3), 209–213.—A review is presented, which includes micro-methods of insulin assay. (83 references.)
D. E. EVANS

783. **Determination of thiamine, riboflavine, pyridoxine and nicotinamide in multivitamin preparations. I. Choice of the methods of determination.** A. W. M. Indemans and H. E. J. Rademakers (Lab. Ned. Apothekers, Utrecht, Netherlands). *Pharm. Weekbl.*, 1960, **95** (12), 377–393.—An investigation of methods for the determination of the separate compounds is described. The following methods are advocated. *Thiamine*—A modification of the fluorimetric method of U.S.P. XV is used, with abs. ethanol to prevent turbidity in the soln. in isobutyl alcohol instead of centrifuging and drying with anhyd. Na_2SO_4. *Riboflavine*—The fluorimetric method of U.S.P. XV is used, the pH being adjusted to 4·8. *Pyridoxine*—The method of Hochberg *et al.* (*J. Biol. Chem.*, 1944, **155**, 109) with 2,6-dibromo-*p*-benzoquinone-4-chlorimine is modified so that the vol. of isopropyl alcohol used is increased to 6 ml and the vol. of buffer decreased to 1 ml. *Nicotinamide*—Holman's method (*Biochem. J.*, 1954, **56**, 513) is used.
M. J. MAURICE

784. **Determination of barbituric acid derivatives with benzyltrimethylammonium hydroxide in an anhydrous medium.** M. Rink and G. Schuster (Pharm. Inst., Univ., Bonn). *Dtsch. ApothZtg*, 1960, **100** (29), 842–845.—0·1N-Benzyltrimethyl-ammonium hydroxide is prepared by dilution of a 35% methanolic soln. with pyridine and ethanol, and standardisation against benzoic acid. The drug (150 to 200 mg) in ethanol, dimethylformamide or pyridine (7 to 10 ml) is titrated in the presence of 2 or 3 drops of one of the following ethanolic indicator soln.—(*i*) thymol blue 0·1%; (*ii*) β-naphthol violet 0·1%, thymol blue 0·1% and phenolphthalein 0·1%; (*iii*) Chromazurol S (C.I. Mordant Blue 29) 0·1%, phenolphthalein 0·1% and thymol blue 0·1%; (*iv*) β-naphthol violet 0·05% and phenolphthalein 0·1%. Suitable solvents and indicators, with the appropriate colour changes, are given for barbituric acid and 21 derivatives, 3 derivatives of thiobarbituric acid, hydantoin and 5,5-diphenylhydantoin.
A. G. COOPER

785. **Rapid method for the analysis of naphazoline in control and stability samples.** L. N. Mattson and R. N. Gaebeler (Scientific Associates Inc., 3755 Forest Park, St. Louis, Mo.). *Drug Standards*, 1960, **28** (3), 77–78.—Mix the sample (*e.g.*, 2 ml of an aq. soln. containing 0·3 mg of naphazoline hydro-chloride) with citrate - phosphate buffer soln. (pH 4·0) (20 ml) and dye soln. [dissolve bromo-phenol blue (200 mg) in H_2O (30 ml) and 0·1N-NaOH (6 ml) and dilute to 250 ml with H_2O] (5 ml), extract with $CHCl_3$ (50 ml in portions) and measure

the extinction of the extract at 402 mμ against a reagent blank. At the same time, construct a calibration curve. The error is ≃ ± 2%. The hydrolytic degradation products 1-naphthylacetylethylenediamine and 1-naphthylacetic acid do not interfere. A. R. ROGERS

786. **Spectrophotometric determination of *N*-substituted phenothiazines and related substances.** J. Budínský, R. Zahradník and M. Chvapil (I Clinic of Obstetrics and Gynaecology, Charles' Univ., Prague). *Českosl. Farm.*, 1960, **9** (6), 299–303.—Spectrophotometric properties of 10 derivatives of phenothiazines were studied and a method was developed for their determination in biological materials and in pharmaceutical preparations. *Procedure*—To the sample (5 ml) add ethyl ether (5 ml) containing 0·1 ml of 30% NaOH soln. and stored in ice in closed test-tubes. Shake, separate the ether layer and determine the extinction at 253 mμ. The mean error is ± 5%. J. ZÝKA

787. **A note on the quantitative ion-exchange separation and chromatographic determination of 4-aminosalicylic acid.** J. L. Lach and J. Cohen (Coll. of Pharm., State Univ., Iowa City). *Drug Standards*, 1960, **28** (3), 65–68.—4-Aminosalicylic acid (**I**) is determined within ± 2 or 3% after separation from its decomposition product *m*-aminophenol (**II**), which is determined with an error of ≃ 10%. *Procedure*—Apply a soln. of the sample (containing 5 mg of **I**) in 5% aq. ethanol to a column of Amberlite IR-4B (OH^- form). Elute **II** with H_2O (250 ml) and determine by measurement of the extinction at 230 or 280 mμ. Elute **I** with 0·5N-NaCl (250 ml) and determine by measurement of the extinction at 265 mμ. A. R. ROGERS

788. **Assay for bithionol [2,2′-thiodi-(4,6-dichlorophenol)] in liquid soaps.** J. B. Matuszak, F. W. Bope and L. E. Harris (College of Pharmacy, Ohio State Univ., Columbus). *Drug Standards*, 1960, **28** (3), 68–72.—The method is a modification of that of Childs and Parks (*cf. Anal. Abstr.*, 1956, **3**, 3183) for the determination of hexachlorophane. The mean recovery is 99·4% with a coeff. of variation of ± 1·6%. The corresponding figures for the slightly more complicated method of van der Pol (*Ibid.*, 1959, **6**, 2762) are 99·7% ± 3·5%. *Procedure*—Dilute the sample (5 g) to 100 ml with 90% methanol. Dilute one 5-ml aliquot to 50 ml with 0·5N-HCl in 90% methanol and another 5 ml to 50 ml with 90% methanol. Measure the difference in the extinctions of the two soln. at 328 mμ and calculate the concn. of bithionol by the use of a calibration curve. The soln. must be protected from direct sunlight. A. R. ROGERS

789. **Methods for the determination of non-aminated hypoglycaemic sulphamides.** [**I.**] P. Mesnard and R. Crockett (Fac. de Méd. et de Pharm., Bordeaux, France). *Chim. Anal.*, 1960, **42** (7), 346–354.—The identification and/or determination of the sulphonamide type of hypoglycaemic sulphamides, *e.g.*, tolbutamide and P607 (*NN′-p*-chlorobenzenesulphonyl-n-propylurea) can be effected spectrophotometrically by (*i*) measuring the extinction at 230 mμ of an ethanolic soln. of the sample (1 to 20 μg per ml); (*ii*) Kjeldahl distillation and photometry of the evolved NH_3; (*iii*) reaction with 3% aq. diacetyl monoxime, followed by addition of *N*-phenylanthranilic acid and measurement of the extinction of the violet soln. at 530 mμ after addition of $K_2S_2O_8$ to destroy the interfering hydroxylamine; the mean error is ≃ 2·5% for concn. of 8 to 270 mg per litre; (*iv*) hydrolysis (0·05 to 0·25 μg) in cold dil. H_2SO_4, followed by condensation of the n-butylamine with either *p*-nitrophenyldiazonium chloride or Na 1,2-naphthaquinone-4-sulphonate, the extinction of the coloured complex being measured at either 512 mμ or 465 mμ, respectively; Beer's law is obeyed, but pH, temp. and time must be strictly controlled at each stage; (*v*) hydrolysis (0·1 to 0·8 μg) in dil. H_2SO_4, followed by condensation with either 1-fluoro-2,4-dinitrobenzene or picric acid, the hydrolysis and condensation being effected concurrently in H_2O-saturated isoamyl acetate.

[**II.**] P. Mesnard and R. Crockett. *Ibid.*, 1960, **42** (8), 381–387.—Two colorimetric methods for use after the reaction with 1-fluoro-2,4-dinitrobenzene or picric acid are described. These reactions have been applied to the determination of tolbutamide in blood and urine. W. J. BAKER
G. BURGER

790. **Contribution to the determination of 1,4-dihydrazinophthalazine [dihydrallazine].** F. Jančík, B. Buděšínský and J. Körbl (Res. Inst. Pharm. and Biochem., Prague). *Českosl. Farm.*, 1960, **9** (6), 304–307.—The course and conditions of the oxidation of dihydrallazine with various oxidising agents were studied. The oxidation with $KBrO_3$ or $K_2Cr_2O_7$ was found to be suitable for volumetric purposes. *Procedures: (i) with $KBrO_3$*—Dissolve the sample (as chloride or sulphate) (0·3 to 0·5 millimole) in 4N-HCl (20 ml), add KBr (3 g) and titrate with 0·1N-$KBrO_3$ potentiometrically. Iodimetric back-titration of an excess of $KBrO_3$ soln. can also be used. The mean error is ≯ ± 0·65%. *(ii) With $K_2Cr_2O_7$*—Dissolve the sample (0·3 to 0·5 millimole) in 10N-H_2SO_4 (25 ml), add 0·1N-$K_2Cr_2O_7$ (25 ml), set aside for 15 min., dilute with H_2O (100 ml), add KI (1 g) and after 5 min. titrate with 0·1N-$Na_2S_2O_3$. The mean error is ≯ ± 0·65%. J. ZÝKA

791. **Evaluation of stilboestrol diphosphate by paper chromatography.** K. Macek and J. Vaníček (Res. Inst. Pharm. and Biochem., Prague). *Českosl. Farm.*, 1960, **9** (6), 309–311.—Solid samples were dissolved in H_2O or ethanol; injection soln. were placed directly on Whatman No. 2 paper; for papers impregnated with formamide, Whatman No. 4 paper was used. *Stilboestrol phosphates*—The sample (≃ 200 μg) was chromatographed with n-butanol - acetic acid - H_2O (4:1:5). The paper was then sprayed with formamide and heated for 30 min. at 105°. For detection a freshly prepared mixture of 15% $FeCl_3$ soln. with 1% $K_3Fe(CN)_6$ soln. (1:1) was used. The excess of the reagent was washed off with H_2O slightly acidified with HCl. A blue spot indicates stilboestrol phosphates. *Stilboestrol*—The sample (≃ 200 μg) and 0·2, 0·5 and 1 μg of stilboestrol were placed on the paper, which was then impregnated with an ethanolic soln. of formamide (50%); $CHCl_3$ was used as developer. After drying, the detection was carried out as described above. Spots of R_F ≃ 0·50 correspond to stilboestrol and can be compared visually with the standard scale. *Inorganic phosphate*—Spots of the sample (500 μg) and 0·5, 1 and 2·5 μg of H_3PO_4 as standards were placed on the paper and developed with n-butanol - acetic acid - H_2O (4:1:5). The separated spots were detected by spraying with a soln. of molybdate (5 ml of 60% $HClO_4$ mixed with 10 ml of N-HCl and 25 ml of 4% ammonium molybdate soln. and diluted with H_2O

to 100 ml). The chromatogram was dried for 5 to 10 min. at 85° and then sprayed with a soln. of ascorbic acid (5%). Blue spots of R_F 0·09 correspond to inorganic phosphate. J. ZÝKA

792. **Paper-chromatographic detection of nitrogen mustard [mustine hydrochloride].** Yoshio Sakurai and Keiichi Itō (Iatrochem. Inst. of Pharmacol. Res. Foundation, 26 Nishigahara 1-chome, Kita-ku, Tokyo, Japan). *Chem. Pharm. Bull., Japan*, 1960, **8** (7), 655–656 (in English).—A more sensitive reagent than Dragendorff's for the detection of mustine hydrochloride (**I**) is described. An ethanol soln. of **I** is spotted on to a chromatographic paper strip, and an alkaline soln. of 6-mercapto-2-naphthol (**II**), prepared immediately before use by treatment of Seligman's reagent [6,6′-dithiodi-(2-naphthol)] with sodium amalgam or alkali, is spotted on to it. After running the chromatogram for 15 to 17 hr. with the upper layer of butanol - acetic acid - water (4:1:5), and drying, the chromatogram is sprayed with 0·5% *p*-diazobenzenesulphonic acid in 50% ethanol. Four pink to orange spots are obtained, identified by running separate chromatograms and spraying with different reagents. The spot with R_F 0·47 is identified as that of the compound of **I** with **II**. This procedure enables 1 μg of **I** to be detected. E. J. H. BIRCH

793. **The identification of common pharmaceutical quaternary nitrogen compounds.** H. Auterhoff and G. Neumann (Inst. f. Pharm. Chem., Tech. Hochschule, Braunschweig, Germany). *Pharm. Zentralh.*, 1960, **99** (6), 271–274.—Separate the quaternary ammonium compounds which contain long-chain substituents ("invert soaps") (*A*) from other quaternary compounds (*B*) by extraction of *A* with $CHCl_3$ from aq. soln. Identify *A* by pptn. of the ferricyanides; by formation of the coloured $CHCl_3$-sol. permanganates; by paper chromatography (*cf.* Holness and Stone, *Analyst*, 1958, **83**, 71); and by paper chromatography of the products of transamination with morpholine (*cf.* Barber *et al.*, *Anal. Abstr.*, 1956, **3**, 1780). Identify *B* by formation of the picrates; by direct paper chromatography; and by paper chromatography of the products of alkaline hydrolysis. Tables of m.p. and R_F values are given. A. R. ROGERS

794. **Spectrophotometric determination of bismuth in an organic solvent. Application to organic and inorganic salts of bismuth in the field of technical pharmaceuticals.** E. Maggiorelli (Ist. Chim. Farm., Firenze, Italy). *Farmaco, Ed. Prat.*, 1960, **15** (6), 384–393.—The method is based on the formation of $HBiI_4$ by the addition of KI (0·2 ml of a 50% soln.) to a soln. of Bi (from 20 to 80 μg) in a mixture of glacial acetic acid (2 ml) and acetone (2 ml), and measurement of the extinction at 490 mμ. The extinction is proportional to concn. over the given range and is 0·345 for 40 μg of Bi. Methods of preparation of suitable soln. from various pharmaceutical preparations and salts of Bi are described in detail. When the use of HNO_3 is necessary to effect dissolution, measurement of the extinction must be made without delay since, in the presence of mineral acids, the extinction increases with time. The maximum error is ± 3%. E. C. APLING

795. **Complexometric analysis of officinal pharmaceuticals.** B. Schmitz (Andreae-Noris Zahn A.-G., Frankfurt-am-Main). *Dtsch. ApothZtg*, 1960, **100** (25), 693–696.—The determination of the Bi content of bismuth metal, carbonate (**I**), subnitrate (**II**), salicylate (**III**), tribromophenoxide (**IV**), subgallate (**V**) and oxychloride (**VI**) is described. *Procedure*—Dissolve 0·3 g of bismuth metal or **I**, or 0·4 g of **II** in 5 ml of HNO_3 with boiling and add 100 ml of hot water. At 50°, add 0·1 g of a 1% trituration of methyl thymol blue in KNO_3 and titrate immediately with 0·1M-EDTA (disodium salt) to a pale red - violet colour. Add 3 ml of aq. NH_3 (10%) and titrate further until the soln. becomes yellow. To determine Bi in **III** or **IV**, shake 0·4 g with 5 ml of HNO_3 for 5 min., add 5 ml of ethyl ether, swirl gently and add slowly to 100 ml of water heated to 60° and titrate as before, ignoring the ppt. Boil 0·4 g of **V** or 0·3 g of **VI** with 2 ml of dil. HNO_3 and exactly 20 ml of 0·1M-EDTA (disodium salt), cool, add 100 ml of water and 4 g of hexamine. Titrate with 0·1M-$ZnSO_4$ in the presence of the indicator until the soln. becomes violet - blue, and then with 0·1M-EDTA (disodium salt) until the soln. becomes yellow. A. G. COOPER

See also Abstracts—**644**, Determination of formaldehyde and hexamine. **730**, Determination of rutin. **766**, Fluorescence of progesterone. **817**, Determination of vitamin-B group. **846**, Continuous extractor for toxicological analysis. **872**, Salicylamide and salicylic acid in aq. soln.

Food

Food and food additives, beverages, edible oils and fats, vitamins.

796. **Ferricyanide reduction method for reducing sugars.** R. I. Mateles (Lab. voor Microbiol., Tech. Hogesch., Delft, Netherlands). *Nature*, 1960, **187**, 241–242.—Oxalic acid is used instead of a gum to peptise the Prussian blue formed in the $K_3Fe(CN)_6$ method for the determination of reducing sugars (*cf.* Folin and Malmros, *J. Biol. Chem.*, 1929, **83**, 115). *Procedure*—Heat the mixture of sugar (*e.g.*, 20 to 300 μg of glucose) and $K_3Fe(CN)_6$ soln. for 15 min. in a boiling-water bath, cool, add Fe^{3+} soln. (5 ml) and 0·8 % aq. oxalic acid soln. (1 ml), dilute to 25 ml, set aside for 15 min. and measure the extinction at 520 mμ. Perform a reagent blank. A. R. ROGERS

797. **Determination of solids in milk and the water content of butter and wine extract, with anhydrous sodium sulphate and kieselguhr as dispersing agents.** V. N. Njegovan and M. Kranjčević (Inst. f. Prüfung u. Kontrolle von Arzneimitteln, Zagreb, Yugoslavia). *Z. anal. Chem.*, 1960, **175** (6), 428–431 (in German).—Anhydrous Na_2SO_4 in a form suitable for the determination of water in milk (*Ibid.*, 1937, **109**, 403) can be prepared by adding 1·5 to 2 ml of water to Na_2SO_4 obtained by heating the decahydrate (11 g) and keeping the damp salt *in vacuo* over conc. H_2SO_4 for 8 hr. Purified kieselguhr is as effective as Na_2SO_4 for the determination of water in milk or butter, but not for the determination in wine extract. For the determination of water in milk, weigh a portion of anhyd. Na_2SO_4 or kieselguhr (≃ 2 g), add 2 ml of homogenised sample, and re-weigh. Mix well, set aside over conc. H_2SO_4 for 8 hr. at 10 torr, and weigh. For the determination of water in butter, melt 15 to 20 g on the water bath at 50°, then cool to 15°, stirring constantly. Weigh out 0·5 g, warm it to 55°, add a weighed amount of Na_2SO_4 or kieselguhr (≃ 2·5 g), mix well, and cool in the desiccator.

Break up the solid mass, set aside over conc. H_2SO_4 for 8 hr. at 10 torr, and weigh.
R. M. ROWLEY

798. **Factors affecting the separation of milk proteins and partially hydrolysed proteins by continuous-flow paper electrophoresis.** R. F. Peterson and L. W. Nauman (E. Reg. Res. Lab., Philadelphia, Pa., U.S.A.). *J. Chromatography*, 1960, **4** (1), 42–51 (in English).—For the best single-passage separation the minimum flow rate of buffer which does not produce distortion of the pattern is used, the voltage and wattage are kept low, and the feed rate is 2 to 4 mg of protein per hr. The method is particularly effective for separating α-, β- and γ-casein, a mixture of α-lactalbumin and β-lactoglobulin, and the peptides formed from β-casein by the action of trypsin. E. C. BUTTERWORTH

799. **Application of gas chromatography to the control of purity of butter.** J. P. Wolff. *Ann. Falsif.*, 1960, **53**, 318–325.—The method may be used to advantage provided that relative and not absolute values are required. It is applicable to C_8 to C_{20} methyl esters prepared by one of two methods. (*i*) Treat 2 g of fatty acids in methanol with H_2SO_4 for 30 min., add water, extract with hexane or light petroleum, and wash the extract free from acid. Remove the solvent and dry under vacuum. (*ii*) Treat 2 to 5 g of neutral fats in methanol with one-twentieth of the theoretical amount of KOH for saponification, at boiling-point for 30 min. Extract and dry as described above. For the chromatography, a column of 2 metres length, filled with brick, saturated with polyoxyethylene adipate, is used. Helium, at a flow rate of 0·4 to 4 litres per hr., is ten times as sensitive as N as carrier. The temp. is selected between 220° and 240° according to chain-length and 0·05 to 1 ml of esters is used. Under these conditions, reproducible results are obtained on arachis, coconut and palm oils. The application of the method to various butters and mixtures of the foregoing oils, and to a light-petroleum extract of biscuits and rolls is discussed. The addition to butter of less than 1·5% of palm oil, 2% of coconut oil or 4% of margarine can be detected, and the method is considered to be as suitable as that of Reichert-Meissl for controlling the purity of butter.
M. A. ELLIS

800. **Paper-electrophoresis method for the identification of raw material used for the manufacture of cottage cheese.** G. Zimmermann (Technion-Israel Inst. of Technology, Haifa). *Mitt. Lebensmitt. Hyg., Bern*, 1960, **51** (3), 151–157 (in German).—Cottage cheese made from high-temp. skim-milk powder can be distinguished from that made from fresh skim milk or fresh full-cream milk. *Procedure*—The whey is expressed from the cheese and filtered, and 6·25 g of $(NH_4)_2SO_4$ is added to 10 ml of whey. The ppt. is dissolved in 1 ml of H_2O (40°), and 6 to 10 μl is transferred to a paper-electrophoresis apparatus. The paper strip is saturated with barbitone buffer (pH 8·6) and dried. The separation of the whey proteins is carried out at 0·3 mA per 10-mm width of the strip for 16 hr. The strip is dried at 105°, coloured according to the standard method described by Durrum (*J. Amer. Chem. Soc.*, 1950, **72**, 2943), washed and dried. Ammonia fumes are applied to make the spots more readily visible. For quantitative determination, the coloured zones are cut into strips 2 mm × 1 cm, and eluted 3 times with 50% methanol which contains 4% of $NaHCO_3$. The extinction of the eluate is determined at 600 mμ. I. DICKINSON

801. **Sand in canned strawberries.** D. Dickinson and T. W. Raven (The Fruit and Vegetable Canning and Quick Freezing Res. Assoc., Chipping Campden, Glos., England). *Analyst*, 1960, **85**, 521–523.—A survey is made of different packs of canned strawberries to relate the sand content to details of canning practice and horticulture. Soil on fresh fruit is determined by washing the fruit and collecting the soil on tared filter-paper, which is then dried and weighed. Sand is determined as the residue removed by a standardised washing procedure, wet-ashed to destroy organic matter and dried and weighed. The average sand content of all cans examined, including those deliberately packed with dirty fruit, was 105 p.p.m. When the packs of dirty fruit and those containing > 200 p.p.m. were excluded the average was 55 p.p.m. The average for all unwashed packs was 220 p.p.m. It is concluded that, if a pack contains < 100 p.p.m. on average and 100 to 200 p.p.m. in not more than 10% of the cans sampled, the canner has probably taken reasonable precautions in washing and selecting the fruit. Such sand contents are unlikely to be noticed by the consumer. A. O. JONES

802. **Determination of isopropyl ether extract in food dyes.** H. Sulser and O. Högl (Lab. des Eidg. Gesundheitsamtes, Bern). *Mitt. Lebensmitt. Hyg., Bern*, 1960, **51** (3), 180–186 (in German).—The method given in AOAC 1955 was examined and further standardisation of the procedure is suggested to overcome the difficulties of obtaining reproducible results. *Procedure*—The dye (10 g) and 200 ml of H_2O are mixed well and filtered through glass wool into a 500-ml separating-funnel, then shaken twice with 100 ml of isopropyl ether for 1 min. The ether is collected in a 300-ml separating-funnel with the washings from the first funnel and the glass wool, and washed several times with 20 ml of H_2O until colourless. The ether extract is transferred to a 600-ml beaker and evaporated on a hot-plate (70° to 80°) to 40 to 50 ml, then transferred to a tared weighing-glass and evaporated to dryness. The residue is dried to constant wt. in a vacuum-desiccator over H_2SO_4; it should be left outside the desiccator for 15 min. before each weighing.
I. DICKINSON

803. **Visible and infra-red spectroscopic determination of trace amounts of silicones in foods and biological materials.** H. J. Horner, J. E. Weiler and N. C. Angelotti (Dow Corning Corp., Midland, Mich., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 858–861.—Two methods are described. In one, the samples are decomposed by wet oxidation and the residues are fused with Na_2CO_3. The melts are dissolved in HCl and the silicon is determined by the molybdenum-blue procedure. In cases where it is desired to identify the type of silicone present, an i.r. technique is used. Preliminary separation of the silicone from the sample by solvent extraction may or may not be necessary, depending on its concn. and on the degree of interference by other sample constituents. Recoveries ranged from 86 to 98% for the colorimetric method on a ground-beef sample, and from 79 to 89% for the i.r. technique on pineapple juice. G. P. COOK

804. **Soluble extract and extraction coefficient of coffee.** P. Navellier, R. Brunin, F. Chassevent and

A. Isaac (Lab. Municipal, Paris). *Ann. Falsif.*, 1960, **53**, 326–336.—The method chosen to determine the water-soluble extract influences the result, and in this study the following procedures are discussed in detail—(*i*) maceration at 20°, (*ii*) digestion at 50°, (*iii*) digestion at 80°, (*iv*) digestion on a water bath, (*v*) decoction for 30 min. at boiling-point, and (*vi*) continuous extraction for 3 hr. Of these, extraction by digestion at 80° gave the most concordant results. The coeff. of extraction is defined as e/E, where e represents the weight of extract determined on a beverage made under standard conditions with a domestic appliance, and E is the amount of extract from the same coffee. The extraction coeff. characterises the method of preparation of a beverage or coffee extract. M. A. ELLIS

805. **Method for the quantitative estimation of roasted date and tamarind in coffee powder.** C. P. Natarajan, R. Balakrishnan Nair, N. Gopalakrishna Rao, C. S. Viraktamath and D. S. Bhatia (Central Food Technol. Res. Inst., Mysore). *Food Sci., Mysore*, 1960, **9** (2), 39–41.—The presence of cyanidin in these two commonly used adulterants was confirmed. A method based on the measurement of this colour has been developed. *Procedure*—The powder (0·5 g) is heated under reflux in a water bath, for 30 min. for date blends and 2 hr. for tamarind blends, with 100 ml of abs. ethanol containing 1 ml of conc. HCl. The soln. is cooled, filtered, made up to volume, and diluted 2·5 times for date blends and 5 times for tamarind blends. The extinctions are measured at 420 and 490 mμ in a Lumetron photo-electric colorimeter. The ratio of the extinctions at 420 mμ and 490 mμ varies according to the percentage of adulterant in the coffee blend; the ratios for pure coffee, date and tamarind were found to be 2·22 to 2·26, 0·8 and 0·8, respectively. Ratios for blends containing various proportions of adulterants are given. The degree of roasting of coffee beans, dates and tamarind does not affect the ratio. I. DICKINSON

806. **Detection of foreign fat in cocoa products.** H. Woidich, H. Gnauer and O. Riedl (Forschungsinst. der Ernährungswirtschaft, Wien, Austria). *Z. LebensmittUntersuch.*, 1960, **112** (3), 184–190.—Various methods for the detection of adulterated fat are discussed and references are given. A new method has been developed for which a commercially available gas chromatograph has been adapted. From the analysis of 350 samples it was found that the natural variations of fatty acids in raw and roasted cocoa beans from different parts of the world did not influence the detection of foreign fat. When additions such as nuts and milk have been made to the cocoa products, the amount of extracted fat due to these additions can be calculated from the proportion of high- to low-mol.-wt. fatty acids. *Procedure*—The fatty acids are isolated and converted into their methyl esters by treatment with diazomethane, or the dry fat (10 mg) is interesterified with methanol and HCl (*cf.* Stoffel *et al.*, *Anal. Abstr.*, 1959, **6**, 3778). Gas-chromatographic separation of the methyl esters is carried out on a column of Apiezon on Celite, with He as carrier gas, at 200° to 240°. (35 references.)
I. DICKINSON

807. **Detection of stabilisation of beer.** K. Silbereisen (Anal. Lab. der Versuchs- und Lehranstalt für Brauerei in Berlin). *Mschr. Brauerei*, 1960, **13** (6), 73–77.—Methods of detection of proteolytic enzymes, protein-precipitants, reducing agents and preservatives added as stabilisers to beer are discussed, with particular attention to the difficulties of drawing definite conclusions as to the presence or absence of these additions. The method of Schultze-Berndt (*Dissert. Tech. Univ. Berlin*, 1955, No. 43) for determining proteolytic activity in beer, depending on the breakdown of a standard haemoglobin solution, was found useful (and is described in detail). According to the results obtained, in conjunction with those of the usual analytical determinations and of tests for pasteurisation and for preservatives, the definite or probable presence or absence of added enzyme is indicated. C. L. HINTON

808. **Spectrophotometric measurement of colour of beer.** G. Krauss, H. Egner and A. Rebmann (Prüfstelle d. Brauerei R. Leicht A.-G., Stuttgart-Waihingen, Germany). *Brauwissenschaft*, 1960, **13** (6), 181–183.—Results obtained in collaborative tests for 28 pale beers by the EBC method are compared with those obtained by measurement at 430 mμ in the Hellige comparator, with corrections (if necessary) for turbidity measured at 700 mμ. The latter method gives satisfactory results. A formula is given for the conversion of spectrophotometric results into EBC units. P. S. ARUP

809. **Analytical chemistry of wine. IX. Voltammetric determination of traces of thallium.** H. Eschnauer and R. Neeb (Anal. Abt. anorg.-chem. Inst., Mainz a. Rhein). *Z. LebensmittUntersuch.*, 1960, **112** (4) 275–280.—The determination of minute traces of Tl by polarography is not possible at the dropping mercury electrode, because the diffusion current is too small compared with the condenser current (Kolthoff and Lingane, "Polarography I," New York, 1952). A voltammetric method in which a mercury-plated platinum wire is used as an electrode, the apparatus and the circuit diagram are described. The organic material in 50 to 100 ml of wine is first destroyed with H_2SO_4 and H_2O_2, and the Tl is extracted with bromide-ether before recording the polarogram. The curve rises to a sharp peak, the height of which is proportional to the concn. of Tl. Approx. $1·5 \times 10^{-2}$ μg of Tl can be determined. I. DICKINSON

810. **Determination of ammoniacal nitrogen and high-molecular-weight nitrogenous substances [in wine] by a cation-exchange method.** V. Dimotaki-Kourakou (Inst. du Vin, Athens). *Ann. Falsif.*, 1960, **53**, 337–348.—Procedures based on the distillation of the wine are liable to error because of the acidity produced by the breaking-down of reducing sugars. The proposed method is slightly longer, but is applicable to sweet wines, musts and grape juice, and is independent of the presence of sugars, organic acids or organic N. *Procedure*—To 50 ml of sample add half the vol. of 0·1N-NaOH required for the titration of 10 ml of wine, and pass the soln. through a column of Amberlite IRC-50 at a rate of 1 drop in 2 sec. Rinse the column with 50 ml of water. Cations (including NH_4^+) are held by the column, whereas amides, polypeptides and amino-acids pass through with the percolate. Pass 50 ml of N-HCl slowly through the column and wash the column with 50 ml of water. Neutralise the eluate and washings to methyl orange with 2N-NaOH, add 40 ml of borate buffer (pH 7) and distil into 10 ml of 0·1N-H_2SO_4; titrate the excess of

acid with 0·1N-NaOH to methyl red. High-molecular-weight nitrogenous substances are determined by the Kjeldahl method on the eluate from a column of Dowex 50, with a similar method.
M. A. ELLIS

811. **Determination of trisaturated glycerides in fats with mercaptoacetic acid [thioglycollic acid].** L. R. Eshelman, E. Y. Manzo, S. J. Marcus, E. A. Decoteau and E. G. Hammond (Iowa State Univ., Ames, U.S.A.). *Anal. Chem.*, 1960, **32** (7), 844–847.—The method is based on the reaction of the unsaturated glycerides with thioglycollic acid. The resulting glycerides are separated from the neutral trisaturated glycerides by extraction of the ammonium salts and ion-exchange treatment. The trisaturated glyceride content is finally measured by weighing, and then determining the iodine value to correct for unchanged fat. The method was applied to 16 fats. G. P. COOK

812. **Trace elements in edible oils. VII. Spectrographic analysis of trace metals.** A. Vioque and M. del Pilar Villagrán (Inst. de la Grasa, Seville, Spain). *Grasas y Aceites*, 1960, **11** (2), 71–78.—The metals are subjected to 'extractive enrichment' by treatment of the HCl extracts of the ash from the oils with diethyldithiocarbamate, 8-hydroxyquinoline and dithizone (*cf.* Pohl, *Anal. Abstr.*, 1954, **1**, 1390) and a spectrographic analysis of the solutions is carried out on carbon electrodes by the method of Kaiser (*Spectrochim. Acta*, 1944, **2**, 1) with Be as internal standard. All samples of olive oil examined contained Fe, Cu, Mn, Al or Zn. L. A. O'NEILL

813. **Rancidity of olive oil. XI. Comparison of different tests for determining the degree of rancidity.** R. Gutiérrez González-Quijano and A. Vargas Romero (Inst. de las Grasa, Seville, Spain). *Grasas y Aceites*, 1960, **11** (2), 67–70.—Various methods for the detection of rancidity *viz*, the peroxide value and the Kreis, Watts and Major, alcoholic KOH and thiobarbituric acid tests, have been compared on a refined olive oil subjected to ageing in an oven at 70°, under ordinary conditions and with accelerated oxidation. Under all conditions there was an initial induction period in which there was no appreciable reaction, followed by a period in which reaction increased rapidly. The agreement between all the tests was generally good.
L. A. O'NEILL

814. **New criterion for differentiation of the unsaponifiable matter of olive oil.** J. Gracián and J. Martel (Inst. de la Grasa, Seville, Spain). *Grasas y Aceites*, 1960, **11** (2), 59–66.—The hydroxyl value of the unsaponifiable matter appears to afford a criterion for olive oils. Although the content of unsaponifiable matter in oils may differ appreciably, the hydroxyl value of the unsaponifiable matter lies within the range 30 to 50 for olive oils, but for esterified oils, or other oils, the value is higher (60 to 100). Results for various mixtures are given.
L. A. O'NEILL

815. **Gas-liquid chromatography of conjugated fatty acids.** N. W. R. Daniels and J. W. Richmond (Spillers Ltd., Technol. Res. Sta., Station Rd., Cambridge, England). *Nature*, 1960, **187**, 55–56.—The effect of alkali isomerisation on the behaviour of polyunsaturated fatty acids has been studied in relation to linoleic (**I**) and linolenic (**II**) acids as found in wheat-flour oil. Unconjugated and conjugated acids were prepared by a standard procedure and methylated with diazomethane. The mixed methyl esters were analysed with a Pye Argon chromatograph with a column packed with 2·3% of polyoxyethylene adipate as stationary phase on 60 to 100-mesh diatomaceous earth. Results show that, after isomerisation, there is a change in the position occupied by the esters of **I** and **II**, the conjugated isomers showing greater retention. Results obtained when 5·9% of Apiezon L grease is used as stationary phase are also given. In view of these results a milder esterification technique is preferred. The lipid material is interesterified with dry methanol in the presence of an acid, followed by extraction and high-vacuum distillation of the methyl esters formed (*cf.* Stoffel *et al.*, *Anal. Abstr.*, 1959, **6**, 3778).
R. A. HENDEY

816. **New method for determining propyl gallate in fats.** S. Bruno and G. Lupoli (Inst. Pharm. Chem. Univ., Bari, Italy). *Farmaco, Ed. Prat.*, 1960, **15** (7), 419–426.—To detect propyl gallate in fats dissolve 10 g of the material in 50 ml of light petroleum (boiling-range 40° to 60°) and extract with 20 ml of 70% ethanol. To 10 ml of the ethanolic extract add 1 ml of 10% KCN soln. In the presence of propyl gallate a red colour turning yellow is obtained. For quant. determination, dissolve 30 g of fat in light petroleum, with gentle warming if necessary, and make up to 100 ml. Extract the soln. with 1·67% ammonium acetate soln. (3 × 25 ml) and finally with 20 ml of H_2O. Pool the extracts and make up to 100 ml with water. (If persistent emulsions are formed add 1 ml of n-octanol before extraction and use 1·67% ammonium acetate soln. in 5% ethanol.) Take 15 to 25 ml of the diluted extract, make up to 30 ml with 1·25% ammonium acetate soln., add 1 ml of 0·4% uranyl nitrate soln. and measure the extinction at 400 mμ. Construct a reference curve by dissolving 0·2 g of propyl gallate (recryst. from ethanol) in 1·25% ammonium acetate soln. and make up to 1 litre. Prepare a series of standards in the same way. The calculated equation for the mean of ten curves was—$Y_c = 0{\cdot}00373 + 0{\cdot}291416X$, Y_c being the absorption at 400 mμ and X the wt. (mg) of propyl gallate in 30 ml of the test soln. The curve is linear up to 1·6 mg of propyl gallate per 30 ml of soln.
J. I. M. JONES

817. **Simple physico-chemical estimation of thiamine, pyridoxine and nicotinamide in presence of riboflavine and panthenol. I.** D. K. Bardhan, R. N. Bhattacharya and S. K. Dutta (Bengal Immunity Res. Inst., Calcutta). *J. Instn Chem. India*, 1960, **32** (2), 86–90.—A column (10 cm × 1 cm) of Decolorite is percolated with warm (60°) 2% NaOH soln. (30 ml), then with water until the percolate has a pH of 7, then with 0·01N-HCl until the pH is ≃ 4, and then with water until the pH is 4 to 5. Clark and Lubs KCl-HCl buffer (pH 2) is then passed through the column until the percolate has a pH of 2. The mixture of vitamins is added followed by 100 ml of buffer. Riboflavine remains on the column and panthenol does not absorb in the u.v. The eluate is assayed by measuring its extinction at 247, 260 and 290 mμ, and from these figures the concn. of vitamins may be calculated. The method is simple and reasonably accurate.

II. D. K. Bardhan, R. N. Bhattacharya and S. K. Dutta. *Ibid.*, 1960, **32** (2), 91–94.—A mixture of the vitamins is separated by paper electrophoresis at 200 V and 10 mA on No. 1

Whatman paper washed with 1% HCl, in Sørensen's Na citrate - HCl buffer (pH 4). The vitamins are located by u.v. light, with a chlorine chamber as filter, and eluted at 36° with 0·01N-HCl for 16 hr. Estimation is by spectrophotometry, the recoveries being 98 to 99%. C. A. SLATER

818. **Polarographic determination of pyridoxal and pyridoxal 5-phosphate.** O. Manoušek and P. Zuman (Polarographic Inst., Czech. Acad. Sci., Prague). *J. Electroanal. Chem.*, 1960, **1** (4), 324–330 (in German).—Two methods are used. In one, polarography is carried out at pH 2 and pH 9; since the height of the pyridoxal wave varies with pH whilst that of the pyridoxal 5-phosphate wave is constant, the decrease in wave height of the mixture of the two compounds at pH 2 is proportional to the pyridoxal concn. Relevant equations are given. Alternatively, the compounds are converted into their oximes. The half-wave potentials in pH 9 barbitone buffer differ by 80 mV so that a direct determination can be made. A 3×10^{-5}M soln. of pyridoxal can be determined in a 50-fold excess of pyridoxal 5-phosphate. Pyridoxol, pyridoxamine and similar compounds do not interfere.
R. M. S. HALL

819. **Determination of ascorbic acid in highly coloured solutions with *N*-bromosuccinimide.** D. F. Evered (Dept. of Chem., Chelsea Coll. of Sci. and Technol., Manresa Rd., London). *Analyst*, 1960, **85**, 515–517.—For soln. containing red pigments (*e.g.*, blackcurrant juice) the sample is diluted with 1% (v/v) aq. acetic acid until it contains 0·4 to 1·0 mg of ascorbic acid per 5 ml. The diluted sample (5 ml) in a test-tube is mixed with 1 ml of glacial acetic acid and 5 ml of 4% (w/v) aq. KI soln. Ethyl ether (3 ml) is added and the liquid is titrated with *N*-bromosuccinimide soln. [a stock soln. containing 200 mg per 100 ml diluted with water (1 + 9)] from a semi-micro burette. The liquid is shaken after each addition of titrant, and the first appearance of the brown colour of liberated iodine in the organic layer indicates the end of the preferential oxidation of ascorbic acid. The titre is corrected for a blank determination made with 5 ml of water and water equal in vol. to the titre replacing the diluted sample. The *N*-bromosuccinimide soln. is standardised against 5-ml aliquots of a standard ascorbic acid soln. With yellow or brown samples, CCl_4 or $CHCl_3$ may be used as the organic phase, the pink colour of iodine in these solvents providing good colour contrast. A. O. JONES

See also Abstracts—**611**, Determination of N. **718**, Moisture and fat in biological materials. **733**, Pyridoxal phosphate in liver. **740**, Nitrogen compounds in maize extracts. **781**, Chlortetracycline in animal tissues. **783**, Determination of vitamin-B group. **796**, Determination of reducing sugars.

Sanitation

820. **Transfer, concentration and analysis of collected air-borne particulates based on ring-oven techniques.** P. W. West, H. Weisz, G. C. Gaeke, jun., and G. Lyles (Louisiana State Univ., Baton Rouge, U.S.A.). *Anal. Chem.*, 1960, **32** (8), 943–946.—The method described can be used to determine rapidly and accurately 2 to 3 μg of particulate material in 1 cubic metre of air. Techniques have been developed for the direct transfer of the sample from various filter media used in the sample-collection devices to the special paper required in the ring oven. K. A. PROCTOR

821. **Separation and characterisation of polynuclear aromatic hydrocarbons in urban air-borne particulates.** E. Sawicki, W. Elbert, T. W. Stanley, T. R. Hauser and F. T. Fox (R. A. Taft San. Engng Center, U.S. Dept. Health, Educ., and Welfare, Cincinnati, Ohio). *Anal. Chem.*, 1960, **32** (7), 810–815.—The benzene-soluble fraction (50 to 100 mg) is mixed with alumina and transferred to a column containing a lower layer of 9 g of alumina and an upper layer of 0·5 g of silica gel, which is then eluted with successive 100-ml volumes of pentane containing 0, 3, 6, 9 and 12% of ethyl ether, respectively. The fractions are then evaporated *in vacuo* at room temp., the residues dissolved in pentane and the u.v. absorption spectrum of each soln. determined from 220 to 450 mμ. The constituents of the fractions are characterised from these and their fluorescence spectra and spectra in the visible region. Further characterisation is made by spectral analysis in H_2SO_4 or by a colour test. The results for the particulates from various communities are very similar; approximately 12 compounds are found consistently in each.
G. P. COOK

822. **Catalytic atmospheric ozone analyser.** F. J. Olmer (Illinois Inst. Technol., Chicago). *Advanc. Chem. Ser.*, 1959, **21**, 87–92.—Ozone concn. is measured by the temp. differential between two thermistors placed in the gas stream. One thermistor is coated with a catalyst for the decomposition of ozone; the other is uncoated. The difference in temp. results in an unbalance in a bridge circuit, the output of which is fed to a recorder. Water, CO, Cl, NO_2, SO_2, org. peroxides, hydrocarbon vapours and combustion smokes at normal concn. in polluted atmospheres do not interfere. CHEM. ABSTR.

823. **Simple sensitive test for compounds containing the cyclopentadiene CH_2 grouping. Application to air pollution.** E. Sawicki, T. W. Stanley and J. Noe (R. A. Taft San. Engng Center, U.S. Dept. Health, Educ., and Welfare, Cincinnati, Ohio). *Anal. Chem.*, 1960, **32** (7), 816–818.—The reaction of 1,2-dinitrobenzene (**I**), 1,4-dinitrobenzene and 1,4-dinitronaphthalene in alkaline soln. with compounds containing the cyclopentadiene CH_2 group gives a stable blue to green colour with maxima ranging from 600 to 750 mμ. Wavelength maxima and identification limit data for the reaction of **I** with 100 fluorene derivatives are tabulated. Confirmation of the presence of fluorene and benzo-[*a*]- and/or -[*b*]-fluorene in airborne particulates was obtained by this method. G. P. COOK

824. **New standard for the determination of the turbidity of water.** S. Petrović, S. Janković and M. Milojević (Lab. San. Tech., Fac. of Civ. Engng, Belgrade). *Bull. Cent. Belge Étud. et Docum. Eaux*, 1960, (114–115), 204–208 (in French).—A stock emulsion for the preparation of turbidimetric standards contains 300 mg of dioctyl phthalate (**I**) per litre of 20% ethanol. It is prepared by dissolving 0·30 g of **I** in ≃ 100 ml of ethanol, and diluting to 1:1 with ethanol and water. Standards are then prepared by dilution of the stock emulsion with 20%

ethanol; a month must be allowed for the stabilisation of each emulsion, which must be stored in a Pyrex-glass bottle with a ground-in stopper.
J. H. WATON

825. **New technique for measurement of low dissolved-air content of water.** D. M. J. P. Manley (The Polytechnic, London, England). *Brit. J. Appl. Phys.*, 1960, **11** (6), 228–229.—The sample is enclosed in a sealed Perspex cell (70 ml) connected to an extensible bellows. An air - gas bubble is formed (by controlled expansion) under the upper Perspex plate and its diameter is measured with a low-power microscope, first (d_1) at max. expansion, *viz*, when the partial pressure (P_1) of gas in the bubble is approx. equal to the saturated gas pressure (P_s) of the water, and then (d_2) after immediately applying a pressure of one atmosphere to the water. The result is calculated from the solubility of the gas and $P_s = P_1 = (d_2)^3/(d_1)^3$ atm. Provided that P_s is $\geq$ 100 torr, the accuracy attained exceeds that of the three usual methods for determining the dissolved-gas content of water. W. J. BAKER

826. **Use of the phenoxide - hypobromite reaction for the determination of ammonia in natural waters.** V. G. Datsko and V. T. Kaplin. *Gidrokhim. Materialy*, 1959, **29**, 230–237; *Ref. Zhur., Khim.*, 1960, (14), Abstr. No. 56,735.—In the phenoxide - hypochlorite determination of NH_4^+, the NaOCl is replaced by NaOBr. In addition to the greater stability of NaOBr, its use increases the sensitivity of the reaction. *Procedure for natural water*—To 100 ml of the sample add 2 ml of a soln. of Na phenoxide stabilised with thiosulphate (dissolve 1 g of $Na_2S_2O_3.5H_2O$ in 100 ml of water, add 9 g of NaOH, and after it has dissolved add 18 g of pure phenol; dilute to 300 ml; the soln. is stable for 2 to 3 months) and 15 ml of NaOBr soln. (1·5% of active Br, 0·6N in free alkali), set aside for 50 min. and measure the extinction or compare the colour of the resulting blue indophenol. At room temp. the colour is stable for 3 hr. The sensitivity of the reaction is 0·01 mg of NH_4^+ per litre. The error is 10% colorimetrically or about 5% photometrically. C. D. KOPKIN

827. **Spectrographic determination of trace elements in natural waters. I. Concentration of nickel, cobalt, silver, copper, vanadium, tin, bismuth, iron, lead and manganese with sodium diethyldithiocarbamate.** I. T. Klimov and V. Ya. Eremenko. *Gidrokhim. Materialy*, 1959, **29**, 254–263; *Ref. Zhur., Khim.*, 1960, (14), Abstr. No. 56,770.—The elements are extracted from the water into $CHCl_3$ with Na diethyldithiocarbamate (**I**) in the presence of ammonium acetate (pH 4·7 to 4·9). The stock soln. of the elements for standardisation contains 5 μg of Cu, Ag, V, Mo and Mn, 10 μg of Cr, Co, Ni and Bi, and 20 μg of Pb and Sn per ml. To stabilise the soln., acetic acid is added, and any ppt. is dissolved by adding HCl. To prepare the base, 2 g of carbon powder is weighed into a quartz dish, 10 ml of satd. K_2SO_4 soln., 0·5 ml of K_2TiF_6 soln. (1 mg of Ti per ml) and 5 drops of glycerol are added, the mixture is evaporated, heated at 600° and ground for 20 or 30 min. in an agate mortar. To 0·5 litre of the sample add 5 ml of 5% ammonium acetate soln. and adjust the pH to 4·7 to 4·9 with 6N-HCl or 6N-NaOH; add 20 ml of $CHCl_3$ and 2 ml of 5% **I** soln., and shake for 2 min. After 4 or 5 further extractions with 10 ml of $CHCl_3$ and 5 ml of **I** soln., filter the combined extracts and remove $CHCl_3$ on the water bath. Take 60 to 90 mg of the base in a crucible, quantitatively transfer the extract residue, evaporate the contents of the crucible to dryness by side heating to avoid the liquid creeping up the walls, then heat at 450° for 15 to 20 min. Quantitatively transfer the contents to a mortar, grind, and place in a cavity (diam. 1·7 mm, depth 6·5 mm and external diam. 2·7 mm) in a carbon electrode. For standardisation, add 1 ml of each standard soln. to the base in the crucible and 1 drop of glycerol for better removal of the material from the crucible walls. Excite the spectrum in an a.c. arc discharge at 14 to 16 amp. with a carbon upper electrode sharpened to a cone, and photograph on a medium spectrograph till the substance has completely burned away. Analysis is carried out from the most sensitive lines in the u.v. region, with Ti as internal standard. The error of the analysis is ± 20%. C. D. KOPKIN

828. **Determination of strontium-90 in samples of water by ion-exchange processes.** H. Knapstein (Landwirtsch. Forschungsanst., Kiel, Germany). *Z. anal. Chem.*, 1960, **175** (4), 255–265 (in German).—If necessary the water sample is evaporated to precipitate SiO_2 and/or filtered. The method then involves adsorption of all cations on Dowex 50-X12 (200 to 400 mesh), elution with ammonium lactate soln. at pH 5·5, which removes all tervalent ions as one group and the alkaline-earth ions thereafter selectively, and pptn. of Sr as $SrCO_3$. The ^{90}Sr is determined after equilibration for 14 days with ^{90}Y and addition of inactive Y as carrier. Recovery of ^{90}Sr is in the range 94·3 to 99·6% for 0·1 to 14 pC per litre. The method is applicable to drinking water and surface waters. J. P. STERN

See also Abstracts—**503**, Nitrite in water. **519**, Ozone in air. **557**, Chloride in water or air. **834**, Nonanol in air. **840**, Titrator for dissolved O in water. **842**, Apparatus for CO_2 in air.

Agricultural analysis

Soil, fertilisers, herbicides, pesticides, animal feeding-stuffs.

829. **Determination of exchangeable sodium, potassium, calcium and magnesium in soils by atomic-absorption spectrophotometry.** D. J. David (C.S.I.R.O., Div. of Plant Industry, Canberra, A.C.T., Australia). *Analyst*, 1960, **85**, 495–503.—The apparatus used is a modification of that previously described (*Ibid.*, 1958, **83**, 655) and the procedure for making atomic-absorption measurements is as previously described. Interference by Al, PO_4^{3-}, silicate and SO_4^{2-} in the determination of Na, K, Ca and Mg in extracts of soils in N-NH_4Cl is investigated. Comparison between Sr and La as suppressors of the combined interference of these ions showed that Sr is the more efficient. The method is sufficiently sensitive for the analysis of 200-ml extracts of 10-g portions of soil with preliminary concentration. With the apparatus described, 0·1 p.p.m. of Na, 0·05 p.p.m. of Mg, 0·1 p.p.m. of K and 0·2 p.p.m. of Ca can be determined. Recoveries of known amounts of these elements were satisfactory. A. O. JONES

830. **The state of copper in various soils and the effects on cultivated plants. I. Serial determination of active copper in soils.** A. Baroccio and A. Saponaro (Staz. Chim.-Agrar. Sperimentale, Roma,

Italy). *Ann. Sper. Agr.*, 1960, **14** (3), 385–400.—Active copper is extracted from soil samples with a 0·05M soln. of the ammonium salt of EDTA, the extract is adjusted to a pH of 8·8 to 9·0, and the Cu is determined colorimetrically with dithio-oxamide after evaporation of the extract and ashing at 450° for 30 min. Comparative results by the proposed method and by the methods of Dole (*Soil Science*, 1952, **73**, 135) and Vermaat and Van der Bie (*Plant and Soil*, 1950, **2**, 260) are reported. The proposed method is rapid and reproducible.

E. C. APLING

831. **Improved rapid determination of nickel in soils and laterites.** A. N. Chowdhury and B. Das Sarma (Geol. Survey of India, Chowringhee Road, Calcutta). *Anal. Chem.*, 1960, **32** (7), 820–821.—The sample (0·1 g) is fused with $KHSO_4$, the melt is treated with N-HCl (5 ml) for 30 min., and the soln. is diluted to 10 ml. The Ni in an aliquot is separated from most other metals by extraction from a soln. containing Na citrate and aq. NH_3 as Ni dimethylglyoxime into benzene - amyl alcohol (4 : 1). The extract is then shaken with 15% KOH soln. and more dimethlylglyoxime to re-extract the Ni into the aq. phase as a stable wine-red compound (air is the oxidising agent). The intensity of colour is matched against standard Ni soln. The max. error is 30% for 50 to 4000 p.p.m. of Ni; from 30 to 40 analyses can be completed in 8 hr. To ensure optimum development of colour, the benzene - amyl alcohol extract must be shaken twice with 10 ml of wash soln. (950 ml of H_2O, 50 ml of amyl alcohol and 10 g of NaCl) to remove the excess of aq. NH_3.

W. J. BAKER

832. **Volumetric determination of small amounts of iron. III.** V. P. Hirsjärvi, B. Salovius and M. Uosukainen (Nat. Agric.-chem. Lab., Helsinki, Finland). *Mikrochim. Acta*, 1960, (4), 534–538 (in English).—The Fe^{III} in low-phosphate feeding mixtures is determined, after wet-ashing, with 0·005N-$HgNO_3$ in 5% HNO_3 in the presence of NH_4SCN. The accuracy on 1 mg of Fe is within ± 1%, but H_2SO_4 causes positive errors increasing with its concn., for which corrections are necessary; Mn, Cu and Co also interfere.

J. P. STERN

833. **Determination of phosphine residues in fumigated grain.** F. Strache (Chem. und Lebensmitteluntersuchungsanst., Hygien. Inst., Hamburg). *Dtsch. LebensmittRdsch.*, 1960, **56** (6), 173–175.—Phosphine is determined by a modification of the Gutzeit test, with development of stains in kieselguhr-charged absorption tubes. The tubes (110 mm × 5 mm int. diam.) are divided into two portions by a filter-plate. The lower section (80 mm) is packed with kieselguhr impregnated with Pb acetate, and the upper portion with kieselguhr impregnated with a mixture of gold chloride and silver nitrate. Both AsH_3 and PH_3 produce violet - black stains, the length of which is proportional to the concn. of the gas (within ± 30%) over the range from 1·6 to 12·0 μg of PH_3 and from 5 to 80 μg of AsH_3. *Procedure*—Place the sample (100 g) in a 250-ml flask carrying a tap-funnel with stem extending to the bottom of the flask and a small spherical condenser connected through the absorption tube to a vacuum pump controlled to withdraw 1 litre in 8 min. Add through the tap-funnel a mixture of methanol (50 ml) and 25% H_2SO_4 (50 ml) and boil gently for 2 min. with the tap-funnel open. Withdraw the flame and continue the air flow for 10 min. A stain less than 2·3 mm long indicates a residue of not more than 50 mg of PH_3 per metric ton. Stain lengths obtained from identical quantities of AsH_3 and PH_3 are in the ratio of 1 : 5·1, so that standard stains may be prepared by treating aliquots of standard arsenic soln. as described, with the addition of granulated zinc (from 10 to 20 g) to the reaction flask. Recovery of PH_3 from 100 g of grain is 70%, so that the stain length obtained from 5 μg of PH_3 in 100 g of grain is equivalent to the stain produced from 23 μg of As_2O_3.

E. C. APLING

834. **Determination of nonanol [3,5,5-trimethylhexan-1-ol] residues in potatoes.** W. F. van Vliet and W. H. Schriemer (Inst. of Storage and Produce of Agric. Products, Bornsesteeg 59, Wageningen, Netherlands). *Nature*, 1960, **187**, 235–236.—A colorimetric method is described for the determination of traces of 3,5,5-trimethylhexan-1-ol (**I**) in air and as residues on potatoes. *Procedure*—Shake samples of air (5 litres) with toluene (50 ml). Peel samples of potatoes (1000 g) and treat peel and tubers separately; suspend in water (2500 ml), distil in steam and extract the distillate (300 ml) with toluene (2 × 25 ml). Mix a 7-ml aliquot of the toluene soln., containing 0·2 to 3 mg of **I**, with solid vanadium 8-hydroxyquinolinate (30 mg), heat for 60 min. in a boiling-water bath, cool for 10 min., filter, dilute to 10 ml and measure the extinction at 375 mμ against a reagent blank. Alcohols naturally present in potatoes also give the colour reaction, and a correction for this must be applied.

A. R. ROGERS

835. **Detection and differentiation of E605 [parathion], methyl-E605 [parathion-methyl] and Chlorthion [*O*-3-chloro-4-nitrophenyl *OO*-dimethyl phosphorothioate].** H. Sperlich (Chem. Landesuntersuchungsanst., Stuttgart). *Dtsch. ApothZtg*, 1960, **100** (27), 774–777.—The named compounds are recovered from insecticidal preparations, biological materials, etc., by extraction with ethanol or with benzene followed by evaporation and dissolution of the residue in ethanol, or by steam-distillation in the presence of tartaric acid and extraction of the distillate with ether. The extract, adjusted to contain 0·5 to 1% of pesticide, is chromatographed on paper impregnated with liquid paraffin, with 70% methanol as solvent. The separated pesticides are detected by reduction with a 1·5% soln. of $TiCl_3$, treatment with aq. NH_3 and HCl, diazotisation by ethyl nitrite or amyl nitrite vapours and coupling with *N*-1-naphthylethylenediamine hydrochloride. Chlorthion is further identified by the colour change of the azo-dye on treatment with H_2O_2. As little as 1 μg of pesticide may be detected.

A. G. COOPER

836. **Colorimetric determination of mepyrium.** D. Monnier, J. Giacometti and R. Aries (Lab. de Chim. Minérale, Univ. Genève). *Mitt. Lebensmitt. Hyg., Bern*, 1960, **51** (3), 187–195 (in French).—Two spectrophotometric methods for the determination of mepyrium [1-(4-amino-2-propyl-5-pyrimidylmethyl)-2-methylpyridinium chloride hydrochloride], used for the treatment of coccidiosis, are described; both are based on the reaction, in alkaline medium, with $K_3Fe(CN)_6$ and naphthalenediol, and measurement of the extinction of the coloured product at 546 mμ. In one, a standard curve is used, and in the other an internal standard. As little as 10 μg of mepyrium can be determined.

I. DICKINSON

837. **Quantitative determination of low concentrations of warfarin in aqueous solution.** J. S. Leahy and C. E. Waterhouse (Nutritional Res. Unit, Huntingdon, England). *Analyst*, 1960, **85**, 492–494.—Ethyl ether is added to the sample soln. (< 6·6 μg per ml) in 0·5N-NaOH, the mixture is acidified with 2N-H_2SO_4 (the amount required being previously determined) and then mechanically shaken for 20 min. The separated aq. layer is re-extracted twice in the same manner. The combined ethereal extracts are shaken by hand successively with 10- and 5-ml portions of 1% $Na_4P_2O_7$ soln., the combined aq. extracts are acidified with 2N-H_2SO_4 and extracted with 3 portions of $CHCl_3$ (10 ml, 10 ml and 5 ml). The extracts are dried overnight with Na_2SO_4 and filtered, the vol. of the filtrate and washings being then reduced to ≃ 5 ml by evaporation. The liquid is applied to an alumina column, the column is washed with ethyl ether under pressure, and then eluted with ethanol acidified with 1% of glacial acetic acid. The extinction of the eluate is measured against the eluent in the range 265 to 315 mμ. Peaks occur at 306, 272 and 283, the last being the highest. The ratio of one peak to the others is characteristic and confirmation that only warfarin is being measured. A. O. JONES

838. **Studies on chemical determination of warfarin and coumachlor and their toxicity for dogs and swine.** H. Wanntorp (State Vet. Med. Inst., Stockholm, Sweden). *Acta Pharm. Tox., Kbh.*, 1959, **16** (2, Suppl.), 5–123.—This survey of the development, pharmacology and toxicology of the coumarin anticoagulants includes a description of a spectroscopic method for the determination of warfarin and coumachlor in animal tissues. The sample is extracted with a mixture of acidified ethanol and ethyl ether, and the extract is washed with dil. H_2SO_4. The compounds are extracted into aq. $Na_4P_2O_7$ soln. and then, after acidification, back into ether. The ether soln. is concentrated and then chromatographed on basic alumina, from which the compounds are eluted with aq. methanol. After partition between ether and aq. $Na_4P_2O_7$ soln., the u.v. absorption curve of the aq. phase is recorded for identification and the compounds are determined by a base-line technique. The calibration curve is rectilinear for up to 20 μg of either compound per ml of soln. W. H. C. SHAW

See also Abstracts—**418**, N in plant material. **507**, Analysis of calcium arsenate.

5.—GENERAL TECHNIQUE AND APPARATUS

General

839. **Report on recommended specifications for microchemical apparatus. Volumetric glassware. Micro-pipettes.** American Chemical Society, Committee on Microchemical Apparatus. *Anal. Chem.*, 1960, **32** (8), 1045–1046.—In this report, specifications are recommended for micro-pipettes (Folin-type), micro washout pipettes, and micro weighing-pipettes (density-type, pyknometer).
K. A. PROCTOR

840. **An automatic titrator as applied to Winkler's method for dissolved oxygen.** J. E. Ridley, D. B. L. Elliott and A. B. Oaten (Water Examn. Dept., Metropolitan Water Board, Rosebery Ave., London). *Analyst*, 1960, **85**, 508–514.—The automatic titrator is described in detail. It is arranged for the Winkler titration for dissolved O in water, but titrates the excess of $Na_2S_2O_3$ with KIO_3 soln. All operations are automatic and results are recorded on a strip chart. In field trials at a reservoir, manual determinations were made for comparison with the automatic determinations, and 94% of the comparisons agreed to within ± 0·1 mg of O per litre and the remainder to within ± 0·2 mg per litre. A. O. JONES

841. **Simple technique for semi-micro volumetric gas analysis.** E. T. Radley (Univ., Columbia, Mo., U.S.A.). *J. Chem. Educ.*, 1960, **37** (7), 360.—A procedure is given for determining the percentage by vol. of one or more components in a mixture by measuring the decrease in length of a column (≃ 40 cm long) of the gas, trapped between two mercury globules in a glass capillary (≃ 2 mm internal diam.) after absorption of the component in a suitable liquid. The absorbent liquid is injected into the column by rolling one of the mercury globules over a film of the liquid in the tube. For determining more than one component, the tube should terminate in a small spherical glass joint to which absorption tubes can be attached.
W. J. BAKER

842. **New gas-absorption device. Its application to titrimetric and conductimetric micro-determinations of carbon dioxide in air.** I. Holm-Jensen (Univ., Aarhus, Denmark). *Anal. Chim. Acta*, 1960, **23** (1), 13–27.—The air sample is drawn upward, at a flow rate up to 15 ml per min., through a spiral glass tube and carries with it a broken stream of 0·005M-$Sr(OH)_2$ containing thymolphthalein. The $Sr(OH)_2$ soln., which is ≃ 0·5 ml in total vol. and is accurately measured, is returned from the top outlet of the spiral for continuous re-circulation. The area of contact between the air and the absorbent liquid is ≃ 150 sq. cm. The discharge of the thymolphthalein colour indicates the end-point. In an alternative design, platinum electrodes are used for conductimetric end-point detection. H. N. S.

843. **Continuous determination of the density of a gas and automatic control of gas mixtures.** A. Pochan. *Chim. Anal.*, 1960, **42** (5), 221–225.—The apparatus consists of a large sealed thermally insulated enclosure containing a sensitive chainomatic balance beam, to one end of which is attached a large block of impervious material of low density and to the other a counterpoise, in the form of a shutter which obscures the light from the two luminous sources of an electronic sensing head. The gas to be measured is admitted to the enclosure through a valve controlled by a cyclic timer. Each gas sample is displaced by the succeeding sample. A barometer is fitted to the enclosure and photoelectric circuits are arranged to operate smaller exit valves so that the pressure in the enclosure always returns to a pre-set value. The position of the photocells is servo-adjusted from a thermistor bridge so that the ratio of pressure to temp. is kept constant. The inclination of the balance beam from the horizontal is a measure of the density of the gas. For automatic control, the flow of one gas in a binary mixture is adjusted so that the density is kept constant. R. M. S. HALL

844. **Improved stirrer and bearing for spinning-band distillation columns.** W. F. Pease, A. H. Gilbert and A. Cahn (Res. and Devel. Div., Lever

Bros. Co., Edgewater, N.J., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 894.—The stirrer described is well balanced and provides effective stirring even when the vol. of liquid has diminished to a few ml. Stirrers fitted precisely into still-pots of different sizes can be made easily from wire loops of the appropriate size. K. A. PROCTOR

845. **Fraction-collector turntable.** A. Banting and R. P. Harpur (Inst. of Parisitology, McGill Univ., Macdonald Coll., P.O., Quebec, Canada). *Chemist Analyst*, 1960, **49** (2), 50–51.—Instructions are given for the construction of a turntable from Meccano parts and a fan motor. The table accommodates 300 test-tubes in a spiral or 29 100-ml cylinders in a circle, and will support a distributed load of 10 kg. Indexing is by means of pins fitted beneath the table, which has two motions, rotation about its axis and linear movement on rails. Each indexing movement takes 1 sec. G. BURGER

846. **A continuous extractor for use in toxicological analysis.** A. S. Curry and S. E. Phang (Home Office Forensic Sci. Lab., Harrogate, England). *J. Pharm. Pharmacol.*, 1960, **12** (7), 437–441.—A continuous extractor is described for use with ethanol under reduced pressure; it is employed for the isolation of barbiturates, alkaloids, glycosides and other poisons from viscera. A. R. ROGERS

847. **Some quantitative remarks on extraction equilibria. IV.** M. Oosting [Ferro Enamels (Holland) N.V., Rotterdam]. *Rec. Trav. Chim. Pays-Bas*, 1960, **79** (6), 627–634 (in English).—Previous studies (*cf. Anal. Abstr.*, 1960, **7**, 3034, 3550, 4044) are extended to derive two new formulae describing (*i*) the total extracted metal-ion fraction when a complex MX is formed, insoluble in both aq. and organic phases, and (*ii*) the case where MX is soluble in the aq. but not in the organic phase. The validity of these formulae is tested by reference to quant. data obtained on experimental extractions of UO_2^{2+} from aq. soln. by means of 8-hydroxyquinoline in $CHCl_3$ in the presence of oxalate and citrate ions. Curves relating total extracted metal ion and pH are given for the experimental and corresponding calculated cases. G. P. MITCHELL

848. **Filter-paper oxidation.** E. L. Lee and D. L. Seaton (Univ. of California Radiation Lab., Livermore, U.S.A.). *Anal. Chem.*, 1960, **32** (7), 889–890.—The method described has been used to separate radioactive particulate matter produced in a nuclear explosion from the filter medium on which the samples were collected. The paper is destroyed by oxidation with atomic oxygen produced by the dissociation of oxygen in a high-voltage a.c. glow discharge. Filter-papers up to 8 in. in diameter can be handled, the papers burning in 1 to 16 hr., depending on the amount of material collected on them. The amount of unburned fibre was always $< 1\%$ of the total residue. K. A. PROCTOR

849. **Fractional thermogravimetric analysis.** P. L. Waters (Coal Res. Sect., C.S.I.R.O., Sydney, N.S.W., Australia). *Anal. Chem.*, 1960, **32** (7), 852–858.—A new technique, which extends the scope of thermogravimetric analysis by providing information on the composition or properties of the volatile matter, is described and applications are discussed. Evidence of the reproducibility and accuracy is presented. K. A. PROCTOR

850. **Studies on organic micro-analysis. XXII. Versatile micro melting-point-determination apparatus provided by an exchangeable polarising microscope.** Keiichiro Hozumi and Nobuko Morita (Pharm. Inst., Med. Fac., Univ., Sakyo-ku, Kyoto). *J. Pharm. Soc. Japan*, 1959, **79** (8), 1028–1034.—An apparatus for melting-point determination with a $\times 10$ magnifying glass interchangeable with a $\times 60$ polarising microscope is described. The apparatus is provided with a hot stage, a voltage adjuster and an optical device for reading the thermometer, assembled on a metal body. The hot stage is comparatively small and the temperature response to voltage variation is rapid. The sample can be observed and the thermometer read at the same time. The apparatus renders the determinations more rapid and accurate. The correction of the observed values is discussed. S. NATORI

See also Abstracts—**605**, Apparatus for combustion of org. compounds. **676**, Polynuclear diaryl ketones in air. **759**, Automatic extraction of phenolic steroids.

Chromatography, ion exchange, electrophoresis

851. **Modification of the Forro radiochromatogram scanner for continuous scanning.** J. A. Demetriou and P. Polamero (Sch. of Med., Univ. of Southern California, Los Angeles, U.S.A.). *Anal. Chem.*, 1960, **32** (7), 895–896.—The modification described allows the scanner to be operated continuously and unattended for periods of up to 5 days. K. A. PROCTOR

852. **Plate height in gas chromatography.** L. C. Giddings, S. L. Seager, L. R. Stucki and G. H. Stewart (Dept. of Chem., Univ. Utah, Salt Lake City, U.S.A.). *Anal. Chem.*, 1960, **32** (7), 867–870.—Experimental evidence of the effect of the eddy diffusion term and of pressure gradients on the equations used to describe plate height has been obtained by using full, half and quarter columns at high inlet to outlet pressure ratios. K. A. PROCTOR

853. **Preparation of gas-chromatographic packings by frontal analysis.** E. D. Smith (The Chemstrand Corp., Decatur, Ala., U.S.A.). *Anal. Chem.*, 1960, **32** (8), 1049.—Difficulties due to non-uniform distribution of the stationary phase on the supporting medium in gas chromatography can be overcome by using the chromatographic principle of 'frontal analysis' to prepare the packing. K. A. PROCTOR

854. **Gas chromatography of solid organic compounds.** C. Hishta, J. P. Messerly, R. F. Reschke, D. H. Fredericks and W. D. Cooke (Bristol Laboratories, Syracuse, N.Y., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 880.—The retention times of solid organic compounds have been greatly decreased, so that chromatograms can be obtained at temp. as much as 250° below their b.p., by using stationary phases at concn. of 0·05 to 0·2% supported on glass microbeads of 200 μ diameter. Samples of a few tenths of a mg are injected as soln. in a volatile solvent. The method seems to be applicable to a wide variety of organic compounds, as chromatograms with retention times of < 20 min. have been obtained for

chrysene at 190°, anthraquinone at 175°, *p*-dibromobenzene at 103° and methyl oleate at 148°. The difficulties due to thermal decomposition of both sample and stationary phase often encountered in high-temp. work are overcome by this technique. K. A. PROCTOR

855. **Sampling method for solid substances in high-temperature gas chromatography up to 500°.** H. E. Dubský and J. Janák (Lab. for Gas Analysis, Czech. Acad. Sci., Brno, Czechoslovakia). *J. Chromatography*, 1960, **4** (1), 1–5 (in English)—In the method described, a few mg of the sample is weighed into a capillary tube made of a low-melting alloy. The tube is introduced into a sampling device where it melts and the sample is carried with the carrier gas into the chromatographic column. The method is more satisfactory than previously described methods, especially for gas chromatography at high temp. Details of the construction of the capillary tubes and diagrams of the sampling device are given. E. C. BUTTERWORTH

856. **Programmed-temperature gas chromatography.** S. Dal Nogare and W. E. Langlois (Polychemicals Dept., E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 767–770.—An equation has been derived for the dependence of solute retention time on the rate of heating, the mass flow rate of the carrier gas, and the starting temp. for linear temp. conditions. Experimental results agree well with those derived by integration by a computer. It has been shown that, under identical conditions, an increase in the stationary-phase polarity increases the retention time of each member of a polar homologous series by the same amount.
K. A. PROCTOR

857. **Retention times in programmed-temperature gas chromatography.** J. C. Giddings (Dept. of Chem., Univ. of Utah, Salt Lake City, U.S.A.). *J. Chromatography*, 1960, **4** (1), 11–20 (in English).—The theoretical analysis described shows the influence of factors such as molecular structure, heating rate and gas velocity on the retention times of various solutes. The retention temp. curve for a homologous series is discussed.
E. C. BUTTERWORTH

858. **Analytical distillation by gas chromatography. Programmed-temperature operation.** F. T. Eggertsen, S. Groennings and J. J. Holst (Shell Devel. Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1960, **32** (8), 904–909.—The method described has been applied to petroleum distillates having a boiling-range of −40° to 400°, and the results agree well with those obtained by a conventional 20-plate distillation. As the effluent hydrocarbons are oxidised and detected as CO_2 by thermal conductivity, response factors are unnecessary for the interpretation of peak areas. An assay can be performed in about 30 min.
K. A. PROCTOR

859. **Polyesters as stationary phases in gas chromatography.** W. Meyer zu Reckendorf (Dept. of Chem. and Chem. Engng, Stanford Univ., Calif., U.S.A.). *Z. anal. Chem.*, 1960, **175** (5), 350–355.—Applications of various commercially available polyesters in the investigation of homologous series such as methyl esters of fatty acids, fatty aldehydes, fatty alcohols and volatile oils are discussed.
E. G. CUMMINS

860. **Solenoid-operated gas sampler for use in gas chromatography.** R. C. Palmer, D. K. Davis and W. Van Willis (Engng Expt. Sta., Georgia Inst. of Technol., Atlanta, U.S.A.). *Anal. Chem.*, 1960, **32** (7), 894–895.—The sampler described overcomes difficulties associated with the use of manually operated gas-sample valves and has been used successfully with commercially available gas chromatographs. K. A. PROCTOR

861. **Versatile ionisation detector for gas chromatography.** R. Teranishi, C. C. Nimmo and J. Corse (W. Reg. Res. Lab., Albany, Calif., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 896.—This modification of the Lovelock β-ray ionisation detector (*Anal. Abstr.*, 1958, **5**, 3208; 1959, **6**, 3297) enables one detector block to be used with either capillary or large columns and to be operated at temp. up to 250°. K. A. PROCTOR

862. **Thermometric monitor for chromatographic streams.** M. Blumer (Exploration and Production Div., Shell Development Co., Houston, Tex., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 772–776.—A minute thermistor probe and differential amplifier are used as a qual. monitor of chromatographic columns. When the area under the direct temp. *vs.* vol. curve is proportional to the amount of sample the method can be used quant., and peak heights and zone widths can be reproduced within ± 2%. K. A. PROCTOR

863. **Continuous antidromic electrophoresis.** S. Natelson, J. B. Pincus, F. J. Annecchiarico and E. Schmerzler (Biochem. Lab., Jewish Hospital, Brooklyn, New York, U.S.A.). *Microchem. J.*, 1960, **4** (2), 145–154.—The separation of 18 common amino-acids has been achieved by moving the paper in the direction opposite to that of ion migration, thus keeping the acids midway between the electrodes until separation is complete. By immersing the paper in cooled CCl_4 for most of the run, evaporation is reduced, so that higher voltages and currents can be used to give faster separations. Diagrams are given.
P. D. PARR-RICHARD

See also Abstract—**758**, Staining of lipoprotein electropherograms.

Optical

864. **X-ray diffractometer gear-changing mechanism.** A. C. Lilly, I. H. Milne, W. T. Caneer and J. A. Dalzell (Gulf Res. and Devel. Co., Harmarville, Pa., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 893.—The mechanical gear-changer described permits the rapid selection of three different gear ratios on the Philips high-angle diffractometer and saves considerable time when a large number of samples requiring scanning at different speeds are involved.
K. A. PROCTOR

865. **Twenty-one new X-ray diffraction powder patterns.** H. G. Norment, P. I. Henderson and R. L. South (Callery Chemical Co., Callery, Pa., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 796–799.—The tabulated values are mostly of boron compounds and have been obtained by both diffractometer and Debye - Scherrer methods. K. A. PROCTOR

866. **Electronic image intensification of X-ray diffraction patterns.** R. E. Thun, J. Johnson, B. H. Krause and E. A. Meredith (IBM Federal Systems Div., Kingston, N.Y., U.S.A.). *Anal. Chem.*, 1960, **32** (8), 939–941.—By using an electronic image converter tube, the intensity of X-ray diffraction patterns can be increased by a factor of 10^3, thus providing a short exposure time in crystal-structure studies. K. A. PROCTOR

867. **A new plane-grating spectrograph.** P. Kröplin (VEB Carl Zeiss, Jena, Germany). *J. Sci. Ind. Res., A, India*, 1960, **19** (7), 308–310 (in English).—This instrument incorporates a plane grating, ruled with 650 lines per mm, and a large concave aluminium mirror, which acts both as collimator and camera lens. The Ebert mounting produces a stigmatic spectrum, with a dispersion of 7·4 A per mm in the first order, in a flat focal plane. The grating is normally blazed between the first and second orders, but the higher orders are available, and an example taken in the fifth order shows the fine structure of the six components of the line Hg 5461 A. A section of the wavelength scale, covering 2000 to 7000 A of the first-order spectrum, can be printed on to the photographic plate, which can be racked automatically. P. T. BEALE

868. **The use of special atmospheres in spectral analysis.** R. Farský (SVÚMT, Prague). *Hutn. Listy*, 1960, **15** (7), 548–552.—The possibility of the use of Ar, Ne, He, mixtures of inert gases with O, and of CO_2, H, O, etc., is discussed with respect to the reactivity of the gas used with the material of the electrodes, and of the thermal conductivity and pressure of the atmosphere used. (19 references.) J. ZÝKA

869. **A study of atomic absorption spectroscopy.** A. C. Menzies (Hilger & Watts Ltd., London, England). *Anal. Chem.*, 1960, **32** (8), 898–904.—Instrumentation, analytical applications and interference problems are discussed. (16 references.) K. A. PROCTOR

870. **Simple thermostatic device for the Beckman DU spectrophotometer.** H. J. Martin and G. Gorin (Dept. of Chem., Oklahoma State Univ., Stillwater, U.S.A.). *Anal. Chem.*, 1960, **32** (7), 892–893.—The device described can be constructed at low cost and provides temp. control to $\pm$ 0·5° in the range 20° to 50°. Up to 40 min. is needed for the temp. of the sample in the cell to reach equilibrium, and, once attained, the temp. can be maintained for at least 1 hr. K. A. PROCTOR

871. **Spectrophotometric acid - base titrations with the use of indicators.** P. Karsten, H. L. Kies and P. de Hoog. *Rec. Trav. Chim. Pays-Bas*, 1960, **79** (6), 610–616 (in English).—The technique described by Higuchi *et al.* (*Anal. Abstr.*, 1957, **4**, 791) for the spectrophotometric end-point determination of acid - base titrations with the aid of indicators has been applied to smaller quantities of titrated substance, of the order of magnitude of 1 milliequiv., and the extent to which the presence of water in the glacial acetic acid, when this is used as solvent, interferes with the determination of the end-point has been studied. The titration curves obtained differ from those of Higuchi in that, near the end-point, the lines are no longer straight, but there is always a straight portion on the curves of sufficient length to make it possible to determine the end-point sharply by extrapolation. With titrations in aq. acetic acid near the end-point the curve turns less acutely; this phenomenon becomes more pronounced with increasing water content, and this tends to make the determination of the end-point less sharp. J. M. JACOBS

872. **A note on the use of multiple regression for spectrophotometric assays involving more than one component.** P. J. Niebergall and A. M. Mattocks (Coll. of Pharm., Univ. of Michigan, Ann Arbor). *Drug Standards*, 1960, **28** (3), 61–64.—A general procedure is described for setting up the equations for the spectrophotometric determination of the concn. of individual components in multicomponent systems. Only one series of standard solutions is prepared, containing arbitrary amounts of each component. From measurements of the total extinction of each solution at wavelengths corresponding to the max. extinction of the individual constituents, it is possible to determine the molar extinction indices with greater precision than by the usual method. It is also possible to detect interaction between components when it affects the extinction. B. J. WALBY

873. **Errors in infra-red absorption analysis due to solute - solvent interactions. II.** W. R. Ward (Distillers Co. Ltd., Hedon, Hull, England). *J. Appl. Chem.*, 1960, **10** (7), 277–281.—Failures of Beer's law are demonstrated for toluene - cyclohexane and picoline - cyclohexane mixtures. With the former system, failure is entirely due to instrumental causes (*e.g.*, finite slit-width effect), but with the latter system it is partially due to molecular interactions. It is recommended that determinations should be checked by comparison with synthetic mixtures as well as with calibration curves. R. M. S. HALL

874. **An incandescent lamp with a mica window for the infra-red region of the spectrum.** E. N. Maleyev. *Optics and Spectroscopy*, 1960, **8** (2), 144; English translation from *Optika i Spektroskopiya*, 1960, **8** (2).—The radiant power output of an incandescent lamp with a mica window is improved by carburising the tungsten filament. This not only increases the filament emissivity but also reduces its vapour pressure, thus allowing the lamp to be operated with higher filament temperature. The spectral intensities of a lamp of the type described and of a conventional Nernst glower are compared over the wavelength range 3 to 8 μ. B. S. COOPER

875. **Heated cell for quantitative infra-red spectrophotometry.** F. J. Linnig and J. E. Stewart (Nat. Bureau of Standards, Washington, D.C., U.S.A.). *Anal. Chem.*, 1960, **32** (7), 891–892.—The cell described has windows 1 in. in diameter and has been designed for use with Perkin-Elmer or Beckman equipment. It has been used mostly between 70° and 90°. K. A. PROCTOR

876. **Standard fluorescence spectrum for calibrating spectrofluorophotometers.** W. H. Melhuish (Inst. Nucl. Sci., D.S.I.R., Lower Hutt, N. Zealand). *J. Phys. Chem.*, 1960, **64** (6), 762–764.—The fluorescence spectrum of quinine bisulphate has been measured in N-H_2SO_4 with a Hilger constant-deviation spectrometer, equipped with a R.C.A. 931-A photomultiplier at the exit slit, and calibrated with a tungsten-filament lamp at a temp. of 2200° K. The fluorescence extends over the range from 390 to 580 mμ, and quinine bisulphate is recommended for calibrating monochromators for use in the measurement of fluorescence and

phosphorescence spectra. The soln. is reasonably stable to visible and near u.v. radiation, re-absorbs very little of its own fluorescence, is not quenched by dissolved air, and has a very high quantum fluorescence efficiency. R. E. E.

877. **Elementary analysis by fluorescence X-ray spectrography. I.** C. Raimbault and G. Baron. *Chim. Anal.*, 1960, **42** (7), 336–345.—The theory of X-ray fluorescence spectroscopy is presented, the usual type of spectrograph is described, and the advantages and limitations of the method are indicated. At present, qual. analyses only are possible, the lower limit of detection being from 0·001 to 0·01%; elements of atomic no. lower than that of Na cannot be successfully detected. The method is rapid and non-destructive of the sample and is particularly useful for distinguishing between the rare-earth elements or, *e.g.*, Ni and Co.

II. G. Baron, J. Favre and C. Raimbault. *Ibid.*, 1960, **42** (8), 388–404.—The technique has been extended to include elements of atomic no. down to 12 (Mg). This is achieved by the use of extremely thin Mylar windows and low air pressure in the optical path to minimise absorption of the very soft K_α radiations and a dispersing crystal of suitably wide lattice spacing (ammonium dihydrogen phosphate for Mg). For measurement of the K_α radiation of the light elements, a proportional gas circulation counter is used. The uses and limitations of the method are discussed with the aid of examples, which include the study of the mechanism of corrosion, determination of metals in fuels, lubricant additives and catalysts and the analysis of cement. W. J. Baker
G. Burger

878. **Gas characteristics of an optico-acoustic gas analyser.** A. O. Sall. *Optics and Spectroscopy*, 1960, **8** (2), 126–128; English translation from *Optika i Spektroskopiya*, 1960, **8** (2).—The influence of the heat-transfer properties of the gas in the chamber of an infra-red gas analyser on the sensitivity of the system is discussed in detail. B. S. Cooper

Electrical

879. **Galvanic cell for determining oxygen in gases containing carbon dioxide.** K. Koyama (Hanford Laboratories Operation, General Electric Co., Richland, Wash., U.S.A.). *Anal. Chem.*, 1960, **32** (8), 1053–1054.—The substitution of saturated $KHCO_3$ soln. for KOH soln. as the electrolyte in the galvanic cell of Hersch (*Instrum. Pract.*, 1957, **11**, 817, 937) allows the cell to be used to record low concn. of O in carbon monoxide, carbon dioxide, nitrogen, hydrogen and helium, and in mixtures of these. K. A. Proctor

880. **The bubbling platinum electrode.** D. Cozzi and P. G. Desideri (Ist. di Chim. Anal. di Trieste e Firenze, Italy). *J. Electroanal. Chem.*, 1960, **1** (4), 301–306 (in English).—A platinum disc, intermittently immersed in the soln. being examined by reason of nitrogen bubbling out of an annular surrounding tube, is described and compared with a dropping-mercury electrode, and is recommended for use in soln. with high redox potentials. The electrode may be of smooth or platinised platinum, according to the type of system being investigated; a redox system that is reversible on a dropping-mercury or a platinised-platinum electrode, *e.g.*, quinhydrone at pH 7, is irreversible on smooth platinum. The current is linear with concn. of quinhydrone, and the proportionality constant is less than with mercury. The Fe^{3+}- and Fe^{3+}-1,10-phenanthroline systems have been studied. R. M. S. Hall

881. **Thin-membrane micro glass-electrode.** M. T. Bush (Dept. of Pharmacology, Sch. of Med., Vanderbilt Univ., Nashville, Tenn., U.S.A.). *Microchem. J.*, 1960, **4** (2), 216–217.—A small Beckman bulb-type glass electrode and its calomel partner are modified to give a means of measuring pH on a small drop of soln. The thin-membrane glass electrode has been described previously (Bedford *et al.*, *J. Amer. Chem. Soc.*, 1933, **55**, 395). A diagram is given. P. D. Parr-Richard

882. **Electrometric pH determination.** R. G. Bates (Nat. Bur. Stand., Washington, D.C., U.S.A.). *Chimia*, 1960, **14** (4), 111–126 (in English).—The validity of the usual definition of pH is discussed. The assignment of pH values to universally accepted standard reference solutions, which are tabulated, and work based on the estimation of the activity coefficient of the chloride ion, are reviewed. A single standardisation is sufficient for the measurement of unknown pH values between 3 and 10 (for soln. $<$0·1M), but for all doubtful cases, including any measurements outside these limits, dual standardisation is essential. Recommendations for an international pH scale are listed. In the discussion of work in aq. soln. of higher ionic strength ($>$ 0·1M), and in non-aqueous and partially aqueous media, the need for a universally acceptable definition of individual ionic activity coefficient is stressed. Electrode systems and conventional and automatic equipment suitable for all laboratory conditions and for industrial pH control are reviewed. (45 references.) E. G. Cummins

883. **Lithium chloride in non-aqueous potentiometric titrations.** E. L. Grove (School of Chem., Univ. Alabama, U.S.A.). *Talanta*, 1960, **4** (3), 205–206.—Lithium chloride has been found to improve the stability of pH meters with glass and calomel electrodes, and to increase the rate of change in potential per increment of titrant near the end-point, in solvent mixtures having high ratios of benzene to methanol, and in dimethylformamide. It is valueless, or even detrimental, in acidic solvents such as glacial acetic acid.
R. M. S. Hall

884. **Reference electrodes and potentials.** G. Milazzo and G. Bombara (Lab. Chim., Ist. Sup. di Sanità, Roma, Italy). *J. Electroanal. Chem.*, 1960, **1** (4), 265–284 (in English).—A critical review is presented of problems relating to reference and comparison electrodes and potentials, including absolute electrode potentials, potentials relative to the standard hydrogen electrode, accuracy of determination of potentials of H, silver - silver chloride and calomel electrodes, activity coeff. of single ionic species, diffusion potentials at liquid junctions; isothermal and non-isothermal temp. coeff. of reference and comparison electrodes and measurements in non-aq. media. R. M. S. Hall

885. **Measurement of half-wave potentials with cylindrical electrodes.** E. Morgan, J. E. Harrar and A. L. Crittenden (Dept. of Chem., Univ. of Washington, Seattle, U.S.A.). *Anal. Chem.*, 1960, **32** (7), 756–758.—Cylindrical electrodes, which do not require shielding, have been used to measure oxidation potentials in cases where mass transfer is

diffusion-controlled. The current - potential relationships obtained are only slightly different from those obtained assuming linear diffusion at short electrolysis times. K. A. PROCTOR

886. **The general equation for the equivalence-point potential in oxidation - reduction titrations.** A. J. Bard and S. H. Simonsen (State Univ., Austin, Tex., U.S.A.). *J. Chem. Educ.*, 1960, **37** (7), 364–366.—A general equation is derived for the equivalence-point potential in all oxidation - reduction reactions in which no additional equilibria are involved. The equation indicates that the equivalance-point potential is a function of the concn. of the reactants and not, as commonly assumed, a simple weighted average of the standard potentials. The equation is applied to the titration of MnO_4^- with Fe^{2+}, of Fe^{2+} with $Cr_2O_7^{2-}$, and of $S_2O_3^{2-}$ with I_3^-. The small corrections for concn. should be taken into account when scaling macro-titrations down to micro-levels. W. J. BAKER

887. **A measuring instrument for potentiometric and dead-stop titrations with transistor amplification.** I. Kerényi. *Magyar Kém. Lapja*, 1960, **15** (7), 329.—A circuit diagram is given for a cheap and easily constructed apparatus that can be used for potentiometric redox titrations with platinum - calomel electrodes, for dead-stop redox titrations in aq. systems and for Karl Fischer titrations with two platinum electrodes. R. E. E.

888. **Potentiometric behaviour of a silver-plated platinum micro-electrode pair.** R. B. Hanselman, G. H. Schade, jun., and L. B. Rogers (Dept. of Chem. and Lab. for Nuclear Sci., Massachusetts Inst. of Technology, Cambridge, U.S.A.). *Anal. Chem.*, 1960, **32** (7), 761–763.—In the titration of silver with iodide, two micro-electrodes of different sizes have been used to produce a derivative-type peak at the end-point. Although instrument-induced polarisation could occur, it was shown that the peak is due to differences in stress corrosion at the two electrodes. K. A. PROCTOR

889. **Reference electrode for potentiometric silver titrations.** G. Matsuyama (Union Oil Co. of California, Brea, U.S.A.). *Anal. Chem.*, 1960, **32** (7), 886.—The electrode described is constructed from commercially available parts and has proved particularly useful for the titration of chloride in the p.p.m. range. K. A. PROCTOR

890. **Use of graphite electrodes as indicators in potentiometric neutralisation titrations.** J. Berčík (Dept. Anal. Chem., Inst. Chem. Technol., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1960, **14** (5), 372–384.—The graphite electrode can be used in conjunction with the S.C.E. in acid - alkali potentiometric titrations, especially in the presence of oxidising compounds, when other types of electrode (except the glass electrode) cannot be used. It has a low internal resistance, so that the e.m.f. can be measured with ordinary apparatus, which is advantageous in, for example, derivative methods. The potential change exceeds that obtained with the hydrogen electrode. The graphite electrode can be activated by immersion in aq. $KMnO_4$ soln. Its robustness and resistance to oxidising and reducing substances permits its use under unfavourable conditions. J. ZÝKA

891. **Micro-range iodimetry by combining precision null-point potentiometry and electrolytic generation of iodine.** H. V. Malmstadt and H. L. Pardue (Dept. of Chem. and Chem. Engng, Univ. of Illinois, Urbana, U.S.A.). *Anal. Chem.*, 1960, **32** (8), 1034–1038.—The method described can be used to determine oxidising or reducing materials in concn. equivalent to 0·5 to 5 p.p.m. of iodine with an accuracy and reproducibility better than 0·02 p.p.m. of iodine. Since sodium thiosulphate is not used as the titrant and standard iodine soln. is not required, a number of the difficulties associated with the iodine - iodide system are avoided. K. A. PROCTOR

892. **Carbon-paste electrodes. Application to anodic voltammetry.** C. Olson and R. N. Adams (Dept. of Chem., Univ. of Kansas, Lawrence, U.S.A.). *Anal. Chim. Acta*, 1960, **22** (6), 582–589 (in English).—The methods of preparation, storage and use of carbon-paste electrodes are given. The carbon paste is made with bromonaphthalene or liquid paraffin and the filled electrodes can be stored under distilled water. The anodic range is in general up to 1·2 V *vs.* the S.C.E. with various media, the level being set when the residual current exceeds 2 μA. Little, if any, treatment of the electrode is in general necessary between determinations. For the same batch of paste, electrode areas can be repeated with an average deviation of peak current of 5·7% for 9 successive days, and for reproducibility of peak current one electrode for 22 days gave an average deviation of 1·84%. R. M. S. HALL

893. **Radiometric titrations.** J. F. Duncan and F. G. Thomas (Univ., Melbourne, Australia). *Proc. Aust. Atomic Energy Symposium*, 1958, 637–643.—In radiometric titrations, a radiotracer is used as an indicator to follow the transfer of material between two phases in equilibrium. The theoretical equations governing the various types of radiometric titrations are derived. They are applied to experimental results on the systems—$^{110}AgNO_3$ titrated against KSCN, KCl and $[Co(NH_3)_5SCN](SCN)_2$; $^{60}CoCl_2$ titrated against Na_2WO_4; $Na_2{}^{185}WO_4$ and $Na_{10}{}^{185}W_{12}O_{41}$ titrated against $CuSO_4$; and Ni and Pb titrated against dithizone in the presence of $^{60}CoCl_2$. A continuous-flow apparatus suitable for radiometric titrations (either of the precipitation or of the solvent-extraction type) is described. CHEM. ABSTR.

894. **Low-background thin-wall flow counters for measuring beta-activity of solids.** D. Lal and D. R. Schink (Scripps Inst. Oceanography, Univ. of California, La Jolla). *Rev. Sci. Instrum.*, 1960, **31** (4), 395–398.—Details are given of the design and performance of small disc-shaped flow counters (active volumes 0·2 to 7 ml, active areas 1·6 to 23 sq. cm). The counter consists essentially of two thin gold-plated Mylar films which form the cathode, between which is a pear-shaped loop of thin tungsten wire forming the anode. The main body of the counter is of Lucite. The counter operates in the Geiger region with a mixture of helium and isobutane. Samples can be mounted close to either window, so as to give a high ratio of counting area to volume. Counting efficiencies for natural K in the range 30 to 47% have been obtained. G. SKIRROW

See also Abstract—**622**, Flame ionisation detector for hydrocarbons.

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångström unit	Å
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher-e, -ic	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
Colour Index	C.I.
concentrated	conc.
concentration	concn.
constant	const.
crystalline / crystallised	cryst.
cubic	cu.
current density	c.d.
cycles per second	c/s
density	ρ
density, relative	d or wt. per ml
dilute	dil.
direct current	d.c.
distilled	dist.
ethylenediaminetetra-acetic acid	EDTA
electromotive force	e.m.f.
equivalent	equiv.
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
hour	hr.
hydrogen ion exponent	pH
infra-red	i.r.
insoluble	insol.
international unit	i.u.
kilogram	kg
kilovolt	kV
kilowatt	kW
liquid	liq.
maxim-um, -a	max.
melting-point	m.p.
microgram	μg (not γ)
microlitre	μl
micromole	μmole
micron	μ
milliampere	mA
milli-equivalent	milli-equiv.
milligram	mg
millilitre	ml
millimetre	mm
millimicrogram	mμg
millimolar	mM
millivolt	mV
minute (time)	min.
molar (concentration)	M
molecul-e, -ar	mol.
normal (concentration)	N
optical rotation	α_λ^t
ounce	oz
parts per million	p.p.m.
per cent.	%
per cent. (vol. in vol.)	% (v/v)
per cent. (wt. in vol.)	% (w/v)
per cent. (wt. in wt.)	% (w/w)
potential difference	p.d.
precipitate (as a noun)	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n_λ^t
relative band speed	R_B
relative humidity	r.h.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]_\lambda^t$
square centimetre	sq. cm
standard temp. and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, Fe^{II}, Mo^{V}. Substanecs in the ionic state are represented by Na^+, Fe^{3+}, Fe^{3+}, etc., for cations and by Cl^-, SO_4^{2-}, PO_4^{3-}, etc., for anions.

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